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Phase Equilibrium for Clathrate Hydrates Formed with Methane, Ethane, Propane, or Carbon Dioxide at Temperatures below the Freezing Point of Water

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This paper reports the three-phase (ice + hydrate + guest-rich vapor) equilibrium pressure−temperature conditions at temperatures (243 to 273) K in the systems of water and each of the following guest gases: methane, ethane, propane, and carbon dioxide. The measurements were also performed for the water-rich liquid + hydrate + guest-rich vapor three-phase equilibrium conditions at temperatures above 273 K. The pressure ranges of the present measurements in the four systems are (0.971 to 2.471) MPa in the methane system, (0.122 to 0.637) MPa in the ethane system, (41.0 to 280.0) kPa in the propane system, and (0.364 to 0.963) MPa in the carbon dioxide system. On the basis of the obtained three-phase equilibrium data, the quadruple points for the ice + water-rich liquid + hydrate + guest-rich vapor were also determined in the respective systems. The measurements were carried out using the batch, isochoric procedure. Fine-grained ice powders with diameters of (1 to 2) mm were used to form the hydrate. The measured data were compared with the corresponding data reported in the literature.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules forming cages that enclose the molecules of substances other than water. Water molecules are called “host molecules”, while the molecules of the other substance are called “guest molecules”. Every clathrate hydrate is thermodynamically stable only at pressures higher than the water + hydrate + guest equilibrium pressure at a given temperature or temperatures lower than the water + hydrate + guest equilibrium temperature at a given pressure. Thus, it is quite important to know the equilibrium pressure−temperature conditions, as they are closely related to the cost of the facilities for the hydrate-based technologies and to the estimation of the distribution of the naturally occurring hydrates.

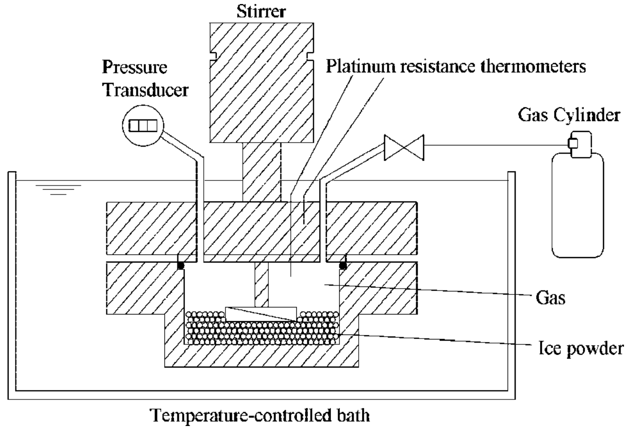

Figure 1. Schematic of the experimental apparatus.

The three-phase equilibrium for clathrate hydrates at temperatures below the freezing point of water (ice (I) + hydrate (H) + guest-rich vapor (V)) is important as related to the following two engineering or scientific topics. The first is the idea of storing and transporting natural gas in the state of clathrate hydrates. The storage and transportation of such hydrates at low temperatures, typically (243 to 273) K, and low pressures, hopefully under atmospheric pressure, have been under consideration for practical application. Because the pressures for dissociation of the hydrates at the temperatures of (243 to 273) K are considered to be higher than atmospheric pressure, we need to anticipate the self-preservation effect for hydrate storage under atmospheric pressure. The self-preservation effect is the apparent, long-term preservation of hydrate crystals under atmospheric pressure, which is lower than the equilibrium pressure for the hydrate. Whether or not we rely on the currently unclarified utility of the self-preservation effect, relevant phase-equilibrium data are essential for designing the process of hydrate-based natural gas storage and transportation. The second is the estimation of the distribution of the naturally occurring hydrates on Earth and in the cosmos. On Earth, naturally occurring hydrates are found in sediments on the seafloor and beneath the permafrost. Air hydrates are found in the Arctic and Antarctic ice sheets.[1] In the cosmos, for example, the existence of clathrate hydrates on Mars and on Titan is theorized. The existence of a carbon dioxide hydrate on Mars has been suggested,[2] while methane hydrate may be a constituent of Titan.[3] As clathrate hydrates often naturally occur at temperatures below the freezing point of water on Earth and in the cosmos, the phase equilibrium data at these temperatures are essential for estimating the distribution of the naturally occurring hydrates. Despite the fact that the phase equilibrium data at temperatures below the freezing point of water are important, there is a paucity of the data,[1,2,4−11] in contrast to the data at temperatures above the freezing point of water for which a large number of studies have been reported. For the accumulation of reliable data at temperatures below the freezing point of water, further measurements are required.

In this paper, we report the phase equilibrium data for clathrate hydrates formed with methane, ethane, propane, and

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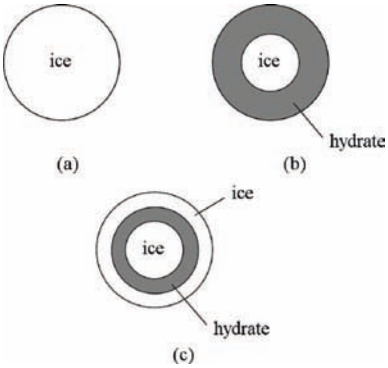

Figure 2. Schematic illustration of hydrate formation and dissociation on an ice particle. (a) Ice particle before hydrate formation. (b) Hydrate crystals formed as a layer covering the ice particle. (c) After the hydrate dissociation at the particle surface. Some of the hydrate crystals were trapped in the particle.

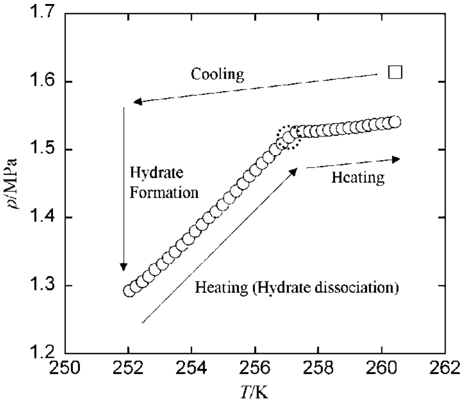

Figure 3. Typical temperature−pressure data obtained for determining phase equilibrium conditions in the methane + ice system. □, initial condition; ○, experimental data. The $p-T$ datum indicated by the dashed circle was employed as the phase equilibrium condition of $p = 1.518$ MPa, $T = 257.1$ K. After the clathrate hydrates are formed, the pressures do not recover to the initial pressure.

Table 1. I + H + V or $\mathrm{L_w}$ + H + V Three-Phase Equilibrium $p-T$ Conditions in a Methane + Water System

T/K	p/MPa	phases in equilibrium
244.2	0.971	I + H + V
245.9	1.041	I + H + V
248.8	1.155	I + H + V
252.9	1.324	I + H + V
256.3	1.485	I + H + V
257.1	1.518	I + H + V
259.1	1.634	I + H + V
262.6	1.829	I + H + V
265.5	2.008	I + H + V
269.1	2.236	I + H + V
272.2	2.471	I + H + V
273.6	2.673	$\mathrm{L_w}$ + H + V
274.7	2.974	$\mathrm{L_w}$ + H + V

carbon dioxide at temperatures below the freezing point of water. The range of the temperatures targeted in the present study is (243 to 273) K that corresponds to the temperatures covered by an ordinary vapor-compression-type refrigeration system. The measurements were also performed for the water-rich liquid + hydrate + guest-rich vapor three-phase equilibrium conditions at temperatures above 273 K in order to validate the present measurement. We also report the data for the quadruple point (ice (I) + water-rich liquid ($\mathrm{L_w}$) + hydrate (H) + guest-rich vapor (V)) based on the experimental data.

Table 2. I + H + V or $\mathrm{L_w}$ + H + V Three-Phase Equilibrium $p-T$ Conditions in a Ethane + Water System

T/K	p/MPa	phases in equilibrium
244.9	0.122	I + H + V
248.4	0.145	I + H + V
252.3	0.177	I + H + V
255.6	0.209	I + H + V
258.4	0.241	I + H + V
261.8	0.281	I + H + V
264.3	0.315	I + H + V
267.3	0.360	I + H + V
269.7	0.403	I + H + V
271.9	0.443	I + H + V
273.9	0.508	$\mathrm{L_w}$ + H + V
275.7	0.637	$\mathrm{L_w}$ + H + V

Table 3. I + H + V or $\mathrm{L_w}$ + H + V Three-Phase Equilibrium $p-T$ Conditions in a Propane + Water System

T/K	p/kPa	phases in equilibrium
245.0	41.0	I + H + V
248.0	48.2	I + H + V
251.2	57.0	I + H + V
254.6	68.1	I + H + V
257.7	79.6	I + H + V
261.0	94.3	I + H + V
264.5	111.9	I + H + V
267.8	132.5	I + H + V
269.2	142.0	I + H + V
272.1	162.7	I + H + V
273.9	194.0	$\mathrm{L_w}$ + H + V
275.5	280.0	$\mathrm{L_w}$ + H + V

Table 4. I + H + V or $\mathrm{L_w}$ + H + V Three-Phase Equilibrium $p-T$ Conditions in a Carbon Dioxide + Water System

T/K	p/MPa	phases in equilibrium
244.5	0.364	I + H + V
247.1	0.406	I + H + V
249.8	0.454	I + H + V
253.0	0.516	I + H + V
256.4	0.593	I + H + V
258.8	0.652	I + H + V
262.7	0.755	I + H + V
263.9	0.790	I + H + V
266.4	0.864	I + H + V
269.4	0.963	I + H + V
273.8	1.312	$\mathrm{L_w}$ + H + V
275.7	1.628	$\mathrm{L_w}$ + H + V

Experimental Section

Materials. The fluid samples used in the experiments were deionized and distilled water: methane of 99.99 vol % certified purity from Takachiho Chemical Industrial, Tokyo; ethane of 99.99 vol % certified purity from Takachiho Chemical Industrial, Tokyo; propane of 99.9 vol % certified purity from Takachiho Chemical Industrial, Tokyo; and carbon dioxide of 99.995 vol % certified purity from Japan Fine Products, Kawasaki. The deionized and distilled liquid water was laboratory made. Ice was formed in a refrigerator from the liquid water.

Apparatus. Figure 1 schematically illustrates the experimental system used to measure the temperature−pressure conditions for the three-phase (ice (I), hydrate (H), and a guest-rich vapor (V)) equilibrium. The main part of the apparatus is the same as employed in our previous study[12] (a stainless steel vessel with a 200 cm^3 inner volume). This vessel is equipped with a magnetic stirrer through its lid to agitate the fluids and hydrate crystals inside the vessel. The vessel is immersed in a temperature-controlled bath to maintain the temperature inside the vessel, T, at a prescribed level. Two platinum resistance thermometers are inserted into the vessel to measure the gas and solid temperatures. The pressure in the vessel, p, is measured

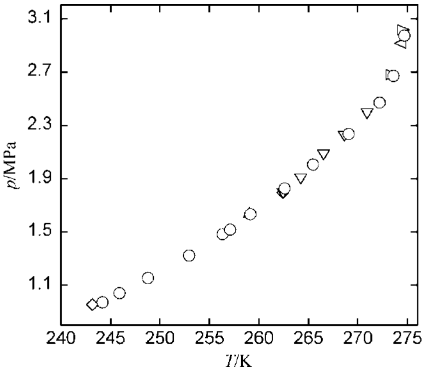

Figure 4. I + H + V or L_w + H + V three-phase equilibrium $p-T$ conditions in a methane + water system. △, Roberts et al.;[4] ▽, Deaton & Frost;[5] ◇, Makogon & Sloan;[9] open arrow pointing right, Ohmura et al.;[22] open arrow pointing left, Nakamura et al.;[23] ○, present study.

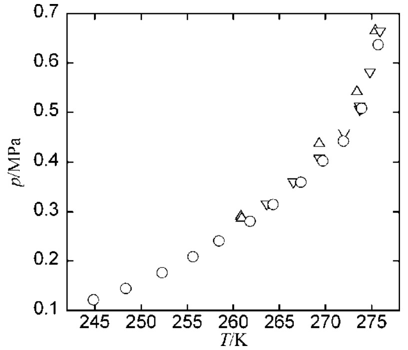

Figure 5. I + H + V or L_w + H + V three-phase equilibrium $p-T$ conditions in an ethane + water system. △, Roberts et al.;[4] ▽, Deaton & Frost;[5] ○, present study.

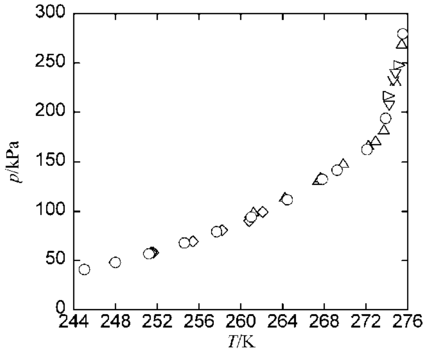

Figure 6. I + H + V or L_w + H + V three-phase equilibrium $p-T$ conditions in a propane + water system. △, Deaton & Frost;[5] ▽, Kubota et al.;[24] ◇, Holder & Godbole;[6] open arrow pointing right, Thakore & Holder;[25] ○, present study.

by a strain-gauge pressure transducer (model PHB-A-5MP, KYOWA Electric Co., Ltd., Tokyo; model PHB-A-1MP-F, KYOWA Electric Co., Ltd.; model VPMR100N, VALCOM Co., Ltd.) depending on the pressure range. The estimated uncertainty of the temperature measurements was ± 0.1 K. The uncertainty of the pressure measurements was ± 11 kPa in the methane system, ± 3 kPa in the ethane system, ± 1.6 kPa for $p < 0.2$ MPa, and ± 3 kPa for $p > 0.2$ MPa in the propane system, and ± 3 kPa for $p < 1.1$ MPa and ± 11 kPa for $p > 1.1$ MPa in the carbon dioxide system. The reliability of the measurements at the temperatures above the freezing point of water using the same apparatus as used in the present study was previously confirmed.[12] The reliability of the measurements at the temperatures below the freezing point of water is discussed in the succeeding sections (see Procedure and Results and Discussion).

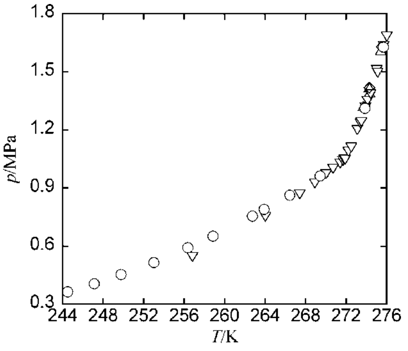

Figure 7. I + H + V or L_w + H + V three-phase equilibrium $p-T$ conditions in a carbon dioxide + water system. △, Deaton & Frost;[5] ▽, Larson;[6] ◇, Adisasmito et al.;[26] ○, present study.

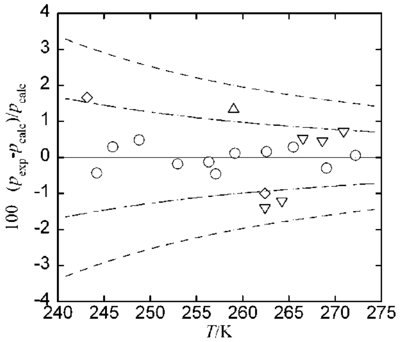

Figure 8. Deviations of the experimental equilibrium pressures in the methane system from those calculated by the empirical correlation determined based on the experimental data in the present study. △, Roberts et al.;[4] ▽, Deaton & Frost;[5] ◇, Makogon & Sloan;[9] ○, present study; dashed line, uncertainty of the present measurement; dash-dotted line, the double of the uncertainty of the present measurement.

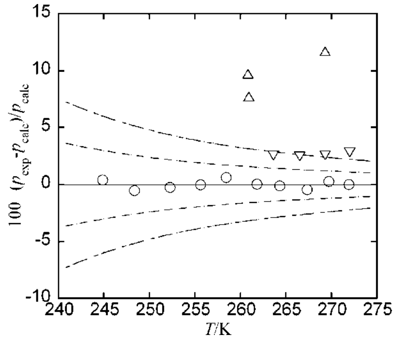

Figure 9. Deviations of the experimental equilibrium pressures in the ethane system from those calculated by the empirical correlation determined based on the experimental data in the present study. △, Roberts et al.;[4] ▽, Deaton & Frost;[5] ○, present study; dashed line, uncertainty of the present measurement; dash-dotted line, the double of the uncertainty of the present measurement.

Procedure. The equilibrium conditions were measured using the batch, isochoric procedure, as described by Danesh et al.[13] Each experimental run was begun by charging the vessel with 30 g of fine-grained ice powders with diameters of (1 to 2) mm. These ice powders were prepared using a pestle and a mortal at a temperature around 220 K. To prevent the charged ice from melting, the vessel was cooled beforehand to about 263 K in the bath. The vessel containing the ice was then immersed in the temperature-controlled bath. The methane, ethane, propane, or carbon dioxide gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel until the pressure inside the vessel, p, had increased to the prescribed level. After T and p had stabilized, the valve in

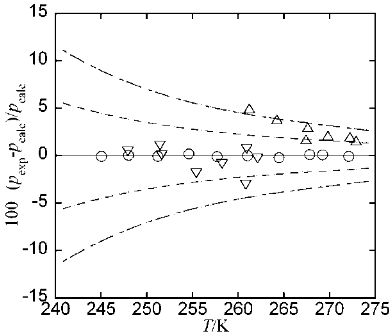

Figure 10. Deviations of the experimental equilibrium pressures in the propane system from those calculated by the empirical correlation determined based on the experimental data in the present study. △, Deaton & Frost;[5] ▽, Holder & Godbole;[6] ○, present study; dashed line, uncertainty of the present measurement; dash-dotted line, the double of the uncertainty of the present measurement.

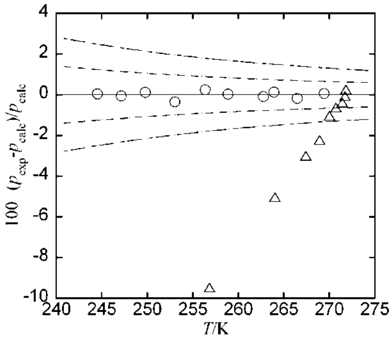

Figure 11. Deviations of the experimental equilibrium pressures in the carbon dioxide system from those calculated by the empirical correlation determined based on the experimental data in the present study. △, Larson;[6] ○, present study; dashed line, uncertainty of the present measurement; dash-dotted line, the double of the uncertainty of the present measurement.

Table 5. Sequential $p-T$ Data Above and Below the Temperature at the I + L_w + H + V Quadruple Point in a Methane + Water System[a]

T/K	p/MPa
271.2	2.410
272.2	2.482
272.4	2.497
272.6	2.514
272.8	2.523
272.9	2.543
273.0	2.570
273.1	2.592
273.3	2.616
273.5	2.666
273.7	2.726
273.9	2.781
274.1	2.834
274.3	2.887
274.5	2.960
274.7	3.016

[a] The data were obtained by the experimental procedure described in the Procedure section.

Table 6. Sequential $p-T$ Data Above and Below the Temperature at the I + L_w + H + V Quadruple Point in an Ethane + Water System[a]

T/K	p/MPa
267.2	0.359
267.4	0.362
267.6	0.366
271.8	0.440
272.0	0.443
272.2	0.448
272.4	0.451
272.6	0.455
272.8	0.459
273.1	0.463
273.2	0.466
273.3	0.475
273.5	0.486
273.7	0.498
273.9	0.512
274.1	0.524
274.3	0.537
274.7	0.568
275.1	0.596
275.5	0.626
275.9	0.658

[a] The data were obtained by the experimental procedure described in the Procedure section.

Table 7. Sequential $p-T$ Data Above and Below the Temperature at the I + L_w + H + V Quadruple Point in a Propane + Water System[a]

T/K	p/kPa
267.8	131
268.3	135
268.8	138
269.3	141
269.8	145
270.3	148
270.8	152
271.2	155
271.8	159
272.0	160
272.2	162
272.5	163
272.6	165
272.8	166
273.1	167
273.3	171
273.5	178
273.7	186
273.9	196
274.1	205
274.3	214
274.5	223
275.0	246
275.4	275
276.0	309

[a] The data were obtained by the experimental procedure described in the Procedure section.

the line was closed. T was then decreased to form the hydrate. If hydrate formation in the vessel was detected by a decrease in p and an increase in T, the temperature of the bath was maintained constant for eight hours, thereby keeping T constant. We then incrementally increased T in steps of 0.2 K. At every temperature step, T was kept constant for (8 to 24) h to achieve a steady equilibrium state in the vessel. In this way, we obtained a $p-T$ diagram for each experimental run, from which we determined a three-phase equilibrium point. If T was increased in the presence of a hydrate, the hydrate partially dissociated, thereby substantially increasing p. After the complete dissociation of the hydrate, only a lower increase in pressure is observed due to the change in the phase equilibria of the fluids in the vessel. Consequently, the point at which the slope of the $p-T$ data plots sharply change was considered to be the point at which all the hydrate crystals dissociate and, hence, was the three-phase equilibrium point. This operation was repeated at several different initial conditions to obtain the three-phase equilibrium data over the specified temperature range. Similar measurements were also performed at temperatures above 273 K to determine the water-rich liquid + hydrate + guest-rich vapor three-phase equilibrium conditions. In these experiments, liquid water was used instead of the ice powder.

Table 8. Sequential $p-T$ Data Above and Below the Temperature at the I + L_w + H + V Quadruple Point in a Carbon Dioxide + Water System[a]

T/K	p/MPa
267.8	0.899
268.8	0.930
269.8	0.963
270.9	0.998
271.1	1.006
271.2	1.012
271.4	1.019
271.5	1.023
271.6	1.025
271.8	1.042
271.9	1.051
272.1	1.074
272.3	1.103
272.5	1.126
272.7	1.154
272.9	1.180
273.3	1.239
273.7	1.294
274.1	1.359
274.6	1.423
275.0	1.501

[a] The data were obtained by the experimental procedure described in the Procedure section.

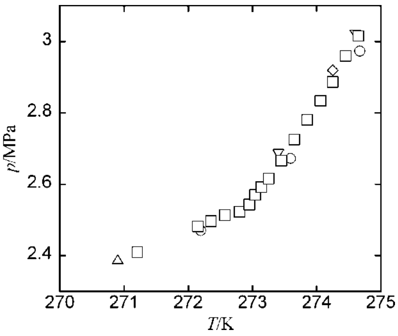

Figure 12. Sequential $p-T$ data above and below the temperature at the I + L_w + H + V quadruple point in a methane + water system. The data were obtained by the experimental procedure described in the Procedure section. △, Deaton & Frost;[5] ▽, Ohmura et al.;[21] ◇, Nakamura et al.;[22] ○, present study; □, present study (sequential data).

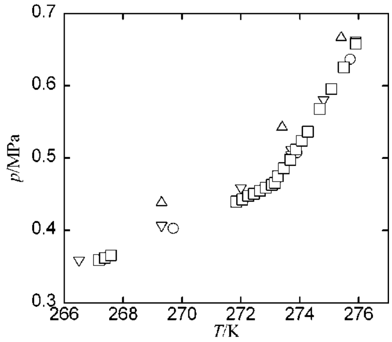

Figure 13. Sequential $p-T$ data above and below the temperature at the I + L_w + H + V quadruple point in an ethane + water system. The data were obtained by the experimental procedure described in the Procedure section. △, Roberts et al.;[4] ▽, Deaton & Frost;[5] ○, present study; □, present study (sequential data).

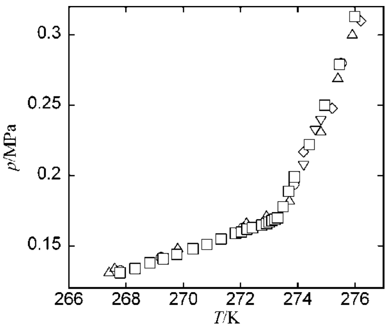

Figure 14. Sequential $p-T$ data above and below the temperature at the I + L_w + H + V quadruple point in a propane + water system. The data were obtained by the experimental procedure described in the Procedure section. △, Deaton & Frost;[5] ▽, Kubota et al.;[24] ◇, Thakore & Holder;[25] ○, present study; □, present study (sequential data).

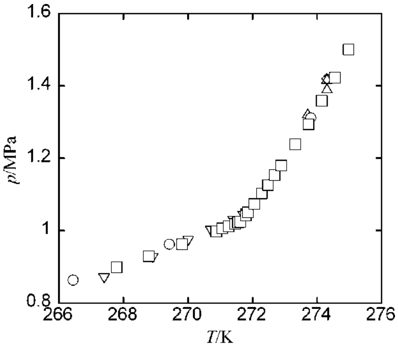

Figure 15. Sequential $p-T$ data above and below the temperature at the I + H + V quadruple point in a carbon dioxide + water system. The data were obtained by the experimental procedure described in the Procedure section. △, Deaton & Frost;[5] ▽, Larson;[6] ◇, Adisasmito et al.;[26] ○, present study; □, present study (sequential data).

Table 9. $p-T$ Conditions at the I + L_w + H + V Quadruple Point in the Systems of Methane, Ethane, Propane, and Carbon Dioxide Hydrate and Theoretical Predictions for the Freezing Point of Water under the Pressure at the Quadruple Point[14-19]

guest gas	T_{exp}/K[a]	p/MPa[b]	T_{theo}/K[c]
methane	272.9 ± 0.2	2.53 ± 0.02	272.87
ethane	273.1 ± 0.2	0.463 ± 0.006	273.09
propane	273.2 ± 0.2	0.170 ± 0.002	273.09
carbon dioxide	271.7 ± 0.2	1.03 ± 0.02	271.72

[a] Experimentally determined temperature for the I + L_w + H + V quadruple point. [b] Experimentally determined pressure for the I + L_w + H + V quadruple point. [c] Theoretical predictions for the freezing point of water under the pressure at the quadruple point.

Additional experiments, which are independent of the above-mentioned experiments for the determination of the three-phase equilibrium conditions, with the following procedure were also performed to confirm the reliability of the measurements in the present study. (1) A large amount of hydrate crystals was formed at a temperature below the freezing point of water. (2) T was incrementally increased in steps of (0.1 to 0.5) K. At every temperature step, T was kept constant for (8 to 24) h to achieve a steady, equilibrium state in the vessel. (3) This stepwise temperature increase was continued to a temperature above that for the quadruple point (I + L_w + H + V), typically ≈ 276 K. (4) The obtained $p-T$ data were compared with the three-phase equilibrium data obtained in the present study. (5) The continuity of the data at the temperatures below and above the freezing point of water was checked. (6) The I + L_w + H + V quadruple point was determined from the data at the temperatures below and above the freezing point of water. This experimentally determined quadruple point temperature was then compared with the freezing point of water[14-19] that is theoretically predicted by considering the effects of the pressure and the gas-in-water solubility.

Results and Discussion

Three-Phase Equilibrium Data. In all the experimental runs for the measurements of the three-phase equilibrium conditions, the pressure did not recover to the initial level after the hydrate formation and dissociation although the temperature did recover to the initial level. A greater difference between the initial and recovered pressures was observed when a large amount of hydrate was formed in the vessel. Specifically, the pressure differences were (2 to 100) kPa depending on the experimental conditions. This deficiency of the recovered pressure to the initial pressure may be ascribed to the so-called self-preservation effect[20] as schematically illustrated in Figure 2. Hydrate crystals should form on the surface of the ice particles as illustrated Figures 2a and b. Decomposition of the once formed hydrate crystals should occur on the surface of the particle. Thus, when a hydrate layer was formed deep in the particle, some of the once-formed hydrate may remain within the particle as illustrated in Figure 2c. The hydrate remaining in the particle would finally dissociate, but this complete hydrate dissociation would require a long time. Thus, in the present study, the duration for each temperature step was less than 24 h. Figure 3 indicates the typical temperature−pressure diagram obtained in the present study from which the three-phase equilibrium conditions were determined to be $p = 1.324$ MPa and $T = 253.0$ K.

The $p-T$ data of the I + H + V three-phase equilibrium in the systems containing methane, ethane, propane, and carbon dioxide are listed in Tables 1 to 4. These data are plotted in Figures 4 to 7. Figures 8 to 11 compare the phase equilibrium data obtained in the present study with those reported in the literature. These figures indicate the deviations of the experimental data obtained in the present study or reported in the literature from the empirical correlation that was determined by best fitting the experimental data obtained in the present study with a third-order polynomial. The definition of the deviation is $100 \cdot (p_{\text{exp}} - p_{\text{calc}})/p_{\text{calc}}$, where p_{exp} is the experimental equilibrium pressure and p_{calcd} is the pressure calculated by the empirical third-order polynomial correlation that was determined on the basis of the experimental equilibrium data obtained in the present study. The uncertainty of the measurements is also indicated in these figures. If the data were plotted within the double of the uncertainty of the present measurements, the data are consistent with the data obtained in the present study within the uncertainty of the measurements. Figure 8 indicates that all of the data reported in the literature for the methane system are consistent with the data obtained in the present study within the uncertainty of the measurements. Figure 9 indicates that the data for the ethane system by Roberts et al.[4] are not consistent with the data obtained in the present study, and the consistency of the data by Deaton & Frost[5] with those in the present study is not necessarily good at temperatures above 267 K. Figure 10 indicates that the consistency of the literature data and those obtained in the present study is good except for the datum by Deaton and Frost[5] at 262 K. Figure 11 indicates that the data reported by Larson[6] are not consistent with those obtained in the present study at temperatures below 270 K. The deviation of Larson's data from those obtained in the present study increases with decreasing temperature. It was previously reported that Larson's data at temperatures above the freezing point of water do not agree with the other corresponding data reported in the literature.[21] The reliability of the data obtained in the present study is discussed in the next section of this paper.

The equilibrium temperature at the corresponding equilibrium pressure of 1.1 MPa or 1 MPa in gauge pressure may be of industrial interest, particularly for Japanese engineers, with regard to the enforcement regulation due to the "High-Pressure Gas Safety Law" in Japan. This temperature is estimated to be 247 K for the methane system on the basis of the data obtained in the present study.

Data Accuracy and Quadruple Point Data. As discussed in the previous section, the three-phase equilibrium data obtained in the present study do not necessarily coincide with the corresponding data reported in the literature. To confirm the reliability of the present measurements, the I + L_w + H + V quadruple point was measured in each of the four systems targeted in the present study. The sequential pressure−temperature data, for the systems with methane, ethane, propane, and carbon dioxide at temperatures above and below that at the quadruple point, that were obtained with the experimental procedure described in the last paragraph of the Procedure section are listed in Tables 5 to 8. Figures 12 to 15 show these sequential data, the corresponding three-phase equilibrium data obtained in the present study as indicated in Tables 1 to 4, and the corresponding data reported in the literature. Table 9 shows the $p-T$ conditions at the quadruple point in the systems of methane, ethane, propane, and carbon dioxide hydrate and the theoretical predictions of the freezing point of water that were effects of the dissolved guest on the water and the freezing point depression by pressure. The comparison of the data indicated in Figures 12 to 15 and in Table 9 indicates the following results: (1) the sequential $p-T$ data coincide well with the three-phase equilibrium data obtained in the present study within the uncertainties of the present pressure and temperature measurements; (2) a good continuity of the sequential data above and below the temperature at the quadruple point was observed; and (3) the experimentally determined temperatures at the quadruple point coincide well with the corresponding theoretical predictions. These results should support the reliability of the measurements in the present study.

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