

# Hydrate Phase Equilibria of the Carbon Dioxide, Methane, and Water System

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Three-phase equilibria for the carbon dioxide + methane + water system were obtained by employing the isobaric temperature search method. Based on these isobaric hydrate equilibrium studies, the ternary hydrate, water-rich liquid, and vapor equilibrium lines generated at different compositions of carbon dioxide and methane were all located between two three-phase equilibrium lines of simple hydrates formed by a single guest component. The upper quadruple points where the four phases hydrate, water-rich liquid, CO<sub>2</sub>-rich liquid, and vapor coexist were measured for the composition range of 100–82.50 mol % carbon dioxide. Below 82.50 mol % carbon dioxide, the upper quadruple points do not exist because none of the components in the vapor phase, neither methane nor carbon dioxide, is able to liquefy at these conditions. In addition, two-phase equilibria of vapor and hydrate were also determined at the three different pressures 20, 26, and 35 bar. Judging from the resulting *T*-*x* diagram, the concentration of carbon dioxide in the hydrate phase was found to be higher than 90 mol % when the corresponding equilibrium vapor-phase composition was more than 40 mol % carbon dioxide. The carbon dioxide concentration and relative selectivity over methane in the hydrate phase appeared to increase with decreasing pressure.

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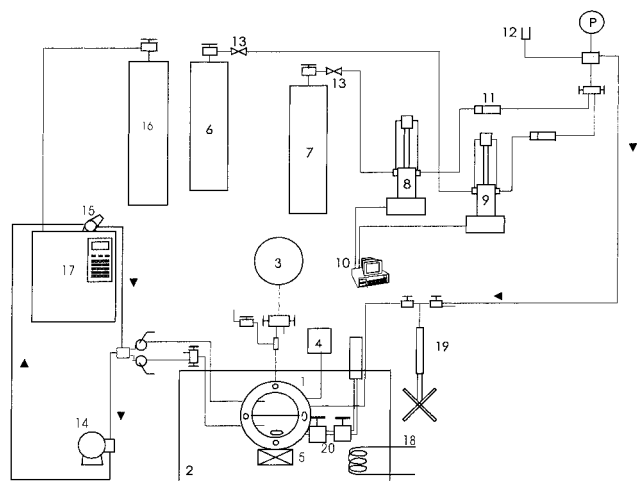
## Introduction

Gas hydrates are crystalline compounds that are formed by physically stable interactions between water and relatively small guest molecules that occupy the cavities built by water molecules. Recently, gas hydrates have attracted the attention of many investigators from all areas of chemical engineering and environmental science from a different perspective. One of the attractive applications of gas hydrates is the sequestration of carbon dioxide in the form of solid hydrates. The suggested strategy is the ocean sequestration of carbon dioxide by direct injection to create a long-lived carbon dioxide hydrate lake on the ocean floor. Vast amounts of natural gas composed of mainly methane and other hydrocarbons have been known to exist in the marine sediments of ocean floors and permafrost zone in a hydrate state.<sup>1</sup> Carbon dioxide hydrates might also form naturally in this region if appropriate conditions of temperature and pressure are provided. Carbon dioxide injection into natural gas hydrate deposits results in the dissociation of methane hydrates. Therefore, it might be reasonable to suggest that carbon dioxide sequestration into marine sediments can be performed simultaneously with natural gas exploitation. To achieve the replacement of methane by carbon dioxide in the hydrate state, determination of the hydrate phase equilibria containing the two guest components carbon dioxide and methane becomes essential. Until now, only a few studies have been carried out that treat this mixture system. Unruh and Katz reported the phase equilibrium data of this mixture and

determined the vapor-phase concentrations indirectly.<sup>2</sup> Berecz and Balla-Achs found that the mixed hydrates of carbon dioxide and methane exhibit instability in the region of carbon dioxide mole fractions of 50% and higher.<sup>3</sup> Adisasmito et al. extended the data of Unruh and Katz and showed that the result of Berecz and Balla-Achs was very unusual.<sup>4</sup> Dholabhai et al. in 1994 measured the three-phase (hydrate, water-rich liquid, and vapor) equilibrium conditions in both pure water and electrolyte solutions containing NaCl, KCl, and CaCl<sub>2</sub>. These electrolytes caused an inhibition effect on hydrate formation.<sup>5</sup> In 1995, Ohgaki et al. measured three-phase equilibria at isothermal conditions and reported the thermodynamic relationship among pressure, gas-phase composition, and hydrate composition. They also briefly discussed the possibility of natural gas exploitation and carbon dioxide isolation.<sup>6</sup> In 1999, Servio et al. measured the incipient equilibrium hydrate formation conditions for two different compositions of 80/20% and 50/50% methane–carbon dioxide mixtures in the presence of neohexane. It was found that the 80/20 gas mixture forms the structure H hydrate. The results from the 50/50 mixture indicate that, above approximately 277.5 K, the structure I hydrate is formed. Below that temperature, a transition state occurs, resulting in structure H or a mixture of structure H and structure I hydrates.<sup>7</sup>

In particular, the isobaric three-phase, hydrate, water-rich liquid, and vapor (H–L<sub>w</sub>–V) equilibrium conditions of carbon dioxide and methane mixtures were measured in this study in order to identify the hydrate-forming stable region. The quadruple points at which the four phases of

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**Figure 1.** Schematic diagram of the experimental apparatus used in this work: 1. equilibrium cell; 2. water bath; 3. pressure gauge; 4. thermocouple; 5. magnetic stirrer; 6. CO<sub>2</sub> cylinder; 7. CH<sub>4</sub> cylinder; 8, 9. syringe pumps; 10. multicontroller; 11. check valve; 12. rupture disk; 13. line filter; 14. high-pressure metering pump; 15. sampling valve; 16. helium gas; 17. gas chromatograph; 18. external heat exchanger; 19. high-pressure pump; 20. sampling port.

hydrate, water-rich liquid, carbon dioxide-rich liquid, and vapor (H–L<sub>w</sub>–L<sub>CO<sub>2</sub></sub>–V) coexist were determined to find the upper limit of the three-phase boundaries. In addition, two-phase equilibria of hydrate and vapor were carefully measured and the concentration of carbon dioxide in the hydrate phase was also analyzed.

### Experimental Section

**Materials.** Methane was supplied by Scientific Gas Products Co. and had a purity of 99.99 mol %. World Gas Co. supplied carbon dioxide with a minimum purity of 99.9 mol %. Water was supplied by Sigma-Aldrich Chemical Co. with a purity of 99.1 mol %. All chemicals were used without further purification.

**Apparatus and Procedure.** A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. The equilibrium cell is made of 316 stainless steel, its internal volume is about 50 cm<sup>3</sup>, and it is equipped with two thermally reinforced sight glasses. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell in the bath. The bath contained about 30 L of a liquid mixture of ethanol and water, whose temperature was controlled by an externally circulating refrigerator/heater. The actual operating temperature in the cell was maintained by a PID temperature controller (JeioTech, MC-31) with an accuracy of ±0.1 K and was measured by a K-type thermocouple probe with a digital thermometer (Cole-Parmer, 8535–26) the resolution of which is ±0.1 K (Every Ready Thermometer Co., Inc). A Heise Bourdon tube pressure gauge (CMM 104957, 0–200 bar range) having a maximum error of ±0.1 bar in the full-scale range was used to measure the cell pressure in the system. For the measurement of vapor compositions at given equilibrium conditions, a sampling valve (Rheodyne, 7413) with a sampling loop of about 24.36 μL was installed and connected on-line to a gas chromatograph (Hewlett-Packard, 5890A) through a high-pressure metering pump (Milton Roy, 2396-31). The gas chromatograph used a thermal conductivity detector (TCD) and a Porapak-Q packed column. A vapor-sampling valve was used to perform the calibration for methane and carbon dioxide. The calibration curves for methane and carbon

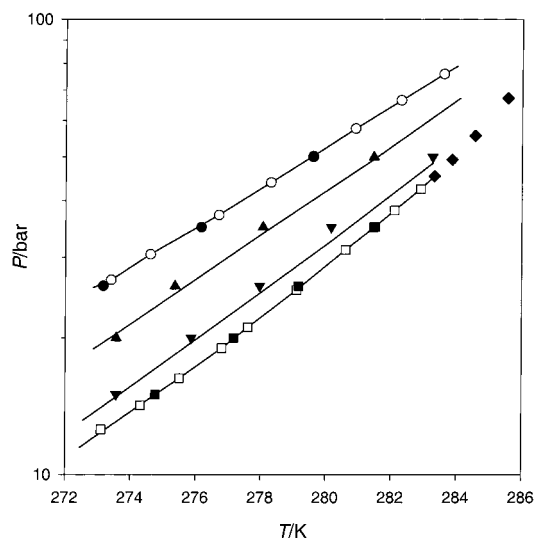
dioxide were fitted to first-order and second-order polynomials, respectively. For measurement of the hydrate compositions, a specially designed sampling port was used to obtain and analyze the hydrate samples at equilibrium conditions. It consists of two valves and a small cylindrical cell. Using the two valves, the hydrate sample was transported into the cylindrical cell and allowed to decompose for analysis. The vapor resulting from the dissociation of the hydrate samples was analyzed using gas chromatography. A carbon dioxide and methane gas mixture was made using two syringe pumps (ISCO Co., D Series). Because the syringe pump has a function of constant-flow operation, the gas mixture with a known composition was introduced into the equilibrium cell, and the constant-pressure mode was also used to maintain isobaric conditions. The charged gas mixture was analyzed using gas chromatography and confirmed to have the desired composition.

Approximately 25 mL of liquid water was initially charged into the equilibrium cell using a metering pump. Then, the mixed gas of carbon dioxide and methane was supplied to the equilibrium cell. After the cell was pressurized to the desired pressure with the gas mixture, the system was cooled to about 5 K below the anticipated hydrate-forming temperature. Hydrate nucleation and growth was then induced, and the system pressure was continuously decreased. The consumed gas mixture was recharged using the high-pressure pump and syringe pump to maintain a constant pressure. After the system pressure reached a steady state, the cell temperature was then very slowly elevated to dissociate the formed hydrates. The cell external heater was used to increase the system temperature at a rate of 1–2 K/h. As the system approached the equilibrium temperature, the dissociation of the hydrate phase caused an increase in the system pressure. To maintain a constant pressure in the system, the decomposed gas was vented through the valve connected to the cell. When the amount of minute crystals and the system pressure remained constant for at least 8–10 h after the system temperature had stabilized, the resulting temperature and pressure were considered as the three-phase equilibrium conditions. When the system pressure and temperature were in equilibrium, the vapor phase was analyzed several times by gas chromatography. The reported equilibrium composition of the vapor phase was taken as the average value.

In particular, the nucleation and dissociation steps were repeated to measure the composition of the hydrate phase. When the system pressure was constant and the temperature was kept constant at 0.5 K below the three-phase equilibrium temperature, the hydrate sample was introduced into the sampling port and analyzed using a gas chromatograph.

### Results and Discussion

Three-phase equilibria (H–L<sub>w</sub>–V) and quadruple points (H–L<sub>w</sub>–L<sub>CO<sub>2</sub></sub>–V) for the binary guest components of carbon dioxide and methane were determined for several isobaric conditions. Measured equilibrium data are presented in Tables 1 and 2 and also shown in Figure 2. The measured equilibrium vapor compositions were very similar to the initial loading compositions. The H–L<sub>w</sub>–V curves of the mixed hydrates were located between those of simple carbon dioxide and methane hydrates. It must be noted, however, that, above 60 mol % CO<sub>2</sub>, the H–L<sub>w</sub>–V curves of the mixed hydrates closely approached that of the simple carbon dioxide hydrate. This phenomenon can be explained



**Figure 2.** Isobaric three-phase (H–L<sub>w</sub>–V) equilibria of the carbon dioxide, methane and water mixtures: ○, Adisasmito et al.<sup>4</sup> (CH<sub>4</sub> hydrate); □, Adisasmito et al.<sup>4</sup> (CO<sub>2</sub> hydrate); ●, this work (CH<sub>4</sub> hydrate); ■, this work (CO<sub>2</sub> hydrate); ▲, this work (*y* = 20 mol % CO<sub>2</sub>); ▼, this work (*y* = 60 mol % CO<sub>2</sub>); ◆, this work (measured upper quadruple points); —, calculated results.

**Table 1.** Isobaric Three-Phase (H–L<sub>w</sub>–V) Equilibrium Data of Carbon Dioxide + Methane + Water Mixtures

<i>P</i> (bar)	<i>T</i> (K)	loading composition (mol % CO <sub>2</sub> )	vapor-phase composition (mol % CO <sub>2</sub> )
15	273.56	60.0	61.69
	274.76	100.0	100.00
20	273.56	20.0	26.34
	275.86	60.0	56.48
	277.16	100.0	100
26	273.16	0.0	0.00
	275.36	20.0	18.54
	277.96	60.0	61.95
	279.16	100.0	100.00
35	276.16	0.0	0.00
	278.06	20.0	20.09
	280.16	60.0	60.87
50	281.46	100.0	100.00
	279.60	0.0	0.00
	281.46	20.0	19.71
	283.26	100.0	59.89

**Table 2.** Upper Quadruple Points (H–L<sub>w</sub>–L<sub>CO<sub>2</sub></sub>–V) of Carbon Dioxide + Methane + Water Mixtures

<i>P</i> (bar)	<i>T</i> (K)	vapor-phase composition (mol % CO <sub>2</sub> )
67.20	285.56	82.50
55.60	284.56	89.93
49.30	283.86	94.83
45.30	283.32	100.00

by comparing the sizes of the guest molecules. Methane molecules can enter both small and large cavities of structure I because of their small size, whereas carbon dioxide molecules can occupy only the large cavities. When structure I is formed with a mixed gas of carbon dioxide and methane, the two species compete with each other for better occupancy. Consequently, carbon dioxide molecules are engaged in most of the large cavities, whereas methane molecules are engaged in small cavities and a small portion of large cavities. Adisasmito and Sloan explained a similar phenomenon.<sup>8</sup> At high carbon dioxide concentrations, the upper quadruple point locus intersects with the H–L<sub>w</sub>–V curve. At an upper quadruple point, one additional CO<sub>2</sub>–

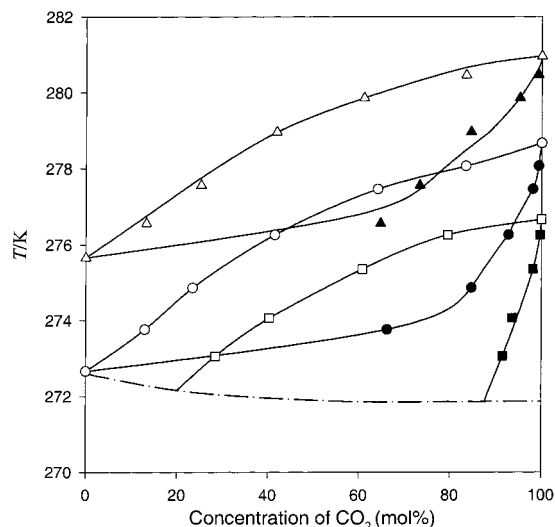
**Table 3.** Optimized Kihara Parameters of Carbon Dioxide and Methane

parameter	CH <sub>4</sub>	CO <sub>2</sub>
$\epsilon/k$ (K)	153.200	168.3
$\sigma$ (Å)	3.2408	2.9925
<i>a</i> (Å)	0.300	0.720

**Table 4.** Two-Phase (H–V) Equilibrium Data of Carbon Dioxide + Methane + Water Mixtures at 20, 26, and 35 bar

<i>P</i> (bar)	<i>T</i> (K)	vapor-phase composition (mol % CO <sub>2</sub> )	hydrate-phase composition (mol % CO <sub>2</sub> )
20	273.06	28.44	91.51
	274.06	40.25	93.63
	275.36	60.76	98.15
	276.26	79.44	99.65
26	273.76	12.93	66.18
	274.86	23.44	84.68
	276.26	41.46	92.72
	277.46	64.11	98.08
35	278.06	83.39	99.35
	276.56	13 0.25	64.72
	277.56	25.23	73.34
	278.96	41.91	88.99
	279.86	61.13	95.23
	280.46	83.44	99.30

rich liquid phase (L<sub>CO<sub>2</sub></sub>) coexists with the hydrate, water-rich liquid, and vapor phases. The upper quadruple locus must terminate at a certain composition where the amount of carbon dioxide is not large enough to liquefy. At temperatures higher than the upper quadruple point temperature, the hydrate phase cannot exist because the quadruple locus becomes the upper limiting condition for hydrate formation. The H–L<sub>w</sub>–V equilibrium pressures were predicted from a thermodynamic model using the van der Waals and Platteeuw model,<sup>9</sup> which relates the chemical potential of water in the hydrate phase to that in a hypothetical empty hydrate lattice. The overall structure of the thermodynamic model for describing H–L<sub>w</sub>–V equilibria was given in detail in our previous work.<sup>10</sup> All of the reference properties of the carbon dioxide and methane hydrates needed for model calculation were obtained from the literature.<sup>11</sup> The optimized Kihara potential parameters were used to describe the interaction between the guest and water molecules in the hydrate cavities and the cavity potential function. These values were optimized from the H–L<sub>w</sub>–V equilibrium data and are presented in Table 3. The Kihara hard-core parameter,  $\alpha$ , is the radius of the spherical core and is given in the literature,<sup>1</sup> whereas the energy and size parameters,  $\epsilon$  and  $\sigma$ , respectively, are determined by regression of the experimental data. The predicted H–L<sub>w</sub>–V results are in good agreement with the corresponding experimental data, as shown in Figure 2. The two-phase equilibria of hydrate and vapor (H–V) measured at three different pressures are given in Table 4 and depicted in Figure 3. When the H–V equilibrium pressure is lower than 25 bar, which is the lower quadruple pressure of pure methane, the H–V equilibrium lines end at the lower quadruple locus. At this lower quadruple locus, the ice phase is newly formed. Therefore, this quadruple locus becomes the lower limiting condition for hydrate formation. As expected, carbon dioxide is more contained in the hydrate phase than methane over the entire range of composition. The concentration of carbon dioxide in the hydrate phase increases as its concentration in the vapor phase increases. When 40 mol % CO<sub>2</sub> exists in the vapor phase, the corresponding carbon dioxide compositions in the hydrate phase were



**Figure 3.** Two-phase (H-V) equilibria of the carbon dioxide, methane, and water mixtures at 20, 26, and 35 bar:  $\Delta$ , vapor phase at 35 bar;  $\blacktriangle$ , hydrate phase at 35 bar;  $\circ$ , vapor phase at 26 bar;  $\bullet$ , hydrate phase at 26 bar;  $\square$ , vapor phase at 20 bar;  $\blacksquare$ , hydrate phase at 20 bar.

found to be 93.63, 92.72, and 88.99 mol % at 20, 26, and 35 bar, respectively. This result indicates that, under lower-pressure conditions, the empty cavities of the hydrates are preferentially occupied by carbon dioxide rather than methane. It is expected that carbon dioxide can create a long-lived hydrate lake on the ocean floor by injection into the natural gas hydrate deposits. Injection of the carbon dioxide stream results in the dissociation of natural gas hydrate, and subsequent growth of carbon dioxide hydrate will occur. Therefore, the formed hydrate phase is occupied mainly by carbon dioxide, and the dissociated methane gas can be recovered as a useful energy source. Using the isobaric  $T$ - $x$  diagram given in this study, a strategy for carbon dioxide sequestration on the ocean floor can be developed.

## Conclusions

The isobaric three-phase (H-L<sub>w</sub>-V) equilibria for mixtures containing the two guest components carbon dioxide and methane were measured. Depending on the composition of the vapor phase, the equilibrium hydrate dissociation pressures were varied between the two H-L<sub>w</sub>-V curves of pure carbon dioxide and methane. The quadruple points where the four phases (H-L<sub>w</sub>-L<sub>CO<sub>2</sub></sub>-V) coexist were also determined to examine the hydrate stability limit. The hydrate phase equilibria were well-predicted by the van der Waals and Platteeuw model. In addition, two-phase equilibria (H-V) were determined at isobaric conditions. When the equilibrium pressure was lowered, the empty cavities of the hydrates were preferentially occupied by carbon dioxide molecules rather than methane molecules over the entire vapor composition range.

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Received for review August 1, 2000. Accepted December 4, 2000. This work was supported by Grant 98-0502-04-01-3 from the Basic Research program of the KOSEF and also partially by the Brain Korea 21 Project.

JE000237A