

## Article

## Formation and Dissociation Processes of Gas Hydrate Composed of Methane and Carbon Dioxide below Freezing

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**Abstract :** The processes of formation and dissociation of gas hydrates were investigated by monitoring pressure and temperature variations in a pressure cell in order to understand the kinetic behavior of gas hydrate and the controlling factors for the phase transition of gas hydrate below freezing. Gas hydrates were made from guest gases (CH<sub>4</sub>, CO<sub>2</sub> and their mixed-gas) and fine ice powder. We found that formation and dissociation speeds of gas hydrates were not controlled by temperature and pressure conditions alone. The results of this study suggested that pressure levels at the formation of mixed-gas hydrate determine the transient equilibrium pressure itself.

**Key words :** gas hydrate, methane, carbon dioxide, kinetics, quasi-liquid layer, self-preservation effect

### 1. Introduction

Gas hydrates are crystalline clathrate compounds composed of water and gases, and are stable at low temperatures and under high-pressure conditions. Enormous amounts of natural gases stored in hydrate crystals in deep-sea sediments and permafrost play an important role as a great reserve of carbon in the world. The question is how natural gas hydrates form, dissociate and are maintained in marine sediments and permafrost. Not only the phase equilibrium of gas hydrates essentially determines their stability, but the supply of gas and water also affect the formation of gas hydrates. Besides, gas hydrates release or absorb a large amount of latent heat due to phase changes and have a direct bearing on their thermal conditions. Sloan (2003) noted that little is known about a kinetic mechanism founded by measurements.

Gas hydrates in permafrost areas exist in conditions where the temperature is below freezing. The pressure conditions, which affect the stability of hydration, are complicated because the hydrate crystals occupy ice or

frozen soil. Yakushev and Chuvilin (2000) proposed that natural gas hydrates exist in areas of subsurface permafrost, where the pressure is lower than the equilibrium value, due to the effects of self-preservation. Although many studies have been carried out to examine the kinetics of hydrate formation and dissociation, little is known about how the gas hydrates form or dissociate at temperatures below freezing. Recently, methods of gas hydrate formation from guest gases and ice particles were adopted in order to understand the kinetic properties of gas hydrate crystallization (e.g., Komai *et al.* 2002; Staykova *et al.* 2002; Wang *et al.* 2002). Fine ice powders are useful in forming gas hydrates from ice because of the large surface area. We also made gas hydrate from ice powders and guest gases in this study.

On the other hand, the kinetic effect on the formation of mixed gas hydrate from ice has not been reported precisely. As natural gas hydrates are composed of mixed gases, each component in the gases may affect kinetics and their maintenance processes. Unruh and Katz (1949) were the first to report the hydrate phase equilibrium of CH<sub>4</sub>, CO<sub>2</sub> and water mixtures. Adisasmito *et al.* (1991), Seo *et al.* (2001) and Seo and Lee (2001) have extended the scope

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on phase equilibrium for the same system. However, these studies dealt with only the system of hydrates, gases and water. In cases where hydrate forms from guest gas and ice, it seems difficult to combine fully with gas and ice during and after hydrate formation. The effect of fractionation between the different gases easily remains in the hydrate phase and finally the formation speed may affect the gas composition in hydrates.

In this paper, pressure and temperature variations during gas hydrate formation and dissociation were measured to understand the kinetic behavior of gas hydrate and to investigate the controlling factors in the phase transition of gas hydrate below the ice point. In addition, fractionation process of the gas mixture ( $\text{CH}_4$  and  $\text{CO}_2$ ) during hydrate formation was reported on a preliminary basis.

## 2. Experimental methods

### Experimental apparatus and materials

A cylindrical pressure cell made of stainless steel (internal dimensions of 40 mm in diameter and volume capacity of  $120 \text{ cm}^3$ ) is durable in terms of internal pressure up to a maximum value of 20 MPa (Fig. 1). Internal temperature and pressure were measured by a platinum thermometer and a pressure gauge (KEYENCE AP-14), respectively. The cell was immersed in a temperature-controlled liquid bath (EYELA NCB-2200) and the temperature was kept below freezing with an accuracy of 0.1 K.

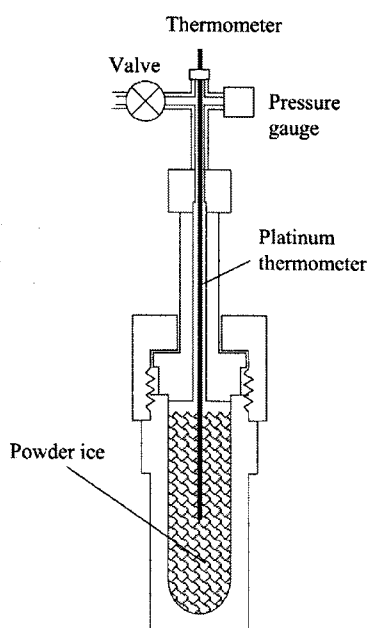


Fig. 1. Schematic of the cylindrical pressure cell.

Samples of gas hydrate were formed from ice powder (mean grain size: less than 0.05 mm) and guest gases ( $\text{CH}_4$ ,  $\text{CO}_2$  and their mixture: 25, 50, 75 mol% $\text{CH}_4$ ) in the pressure cell.  $\text{CH}_4$  (purity: 99.999 vol%) and  $\text{CO}_2$  (purity: 99.999 vol%) were supplied by Takachiho Chemical Industry CO., Ltd. Ice powder was made from water purified by distillation and deionization (ADVANTEC GSH-210), and obtained by shaving an ice sample using microtome.

### Procedure

About 35 g of ice powder was added to the pressure cell and guest gas was charged only once for several seconds over an anticipated equilibrium pressure, which was calculated by CSMHYD Hydrate Program (Sloan 1998), at a controlled temperature. The temperature of the liquid bath was kept constant for each experiment in the range of 260.9–272.6 K. After closing the valve, the pressure continued to decrease to the equilibrium value due to the formation of gas hydrate. Formation time is defined as the period in which the internal pressure decreases and reaches the equilibrium value. Pressure difference  $\Delta P$  is also defined as the difference between actual and equilibrium pressures, which corresponds to the degree of supercooling for hydrate formation.  $\Delta P$  was established in the range of 0.18–1.8 MPa.

Besides, the gas was discharged or recharged from the equilibrium condition and hydrate started to dissociate or form, respectively. Formation and dissociation times are defined as the periods that the phase transition proceeds and the pressure difference from the equilibrium value reaches less than 0.01 MPa. Formation and dissociation speeds ( $\text{mol hour}^{-1}$ ) are obtained from each formation/dissociation time and the amounts of consuming/releasing gas, respectively. In these cases,  $\Delta P$  corresponds to the value of discharged/recharged pressure and was established in the range of 0.05–0.56 MPa. Time variations of pressure and temperature were recorded every 30 seconds automatically.

## 3. Results and discussion

### Initial formation of gas hydrate from ice powder and gas

In all cases the pressure in the cell started to decrease immediately after supplying the gas, and the temperature increased due to the heat of hydrate formation. This indicates that the induction time of hydrate formation from gas and ice is very short and gas hydrate can be formed immediately from gas and ice. Fig. 2 shows the example of time variation on internal pressure and temperature during the formation

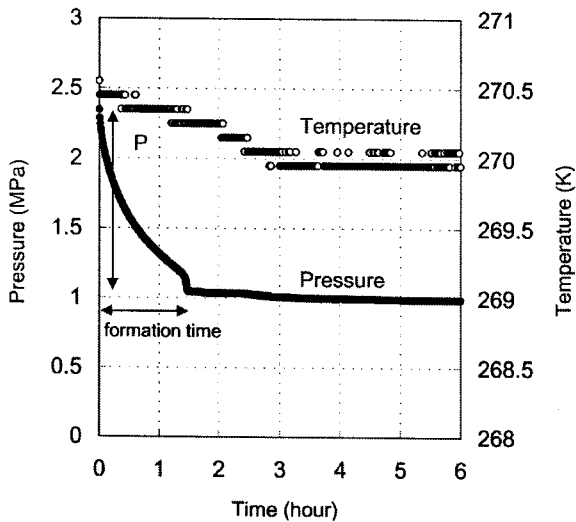


Fig. 2. An example of time variation of the internal pressure and temperature in the formation of CO<sub>2</sub> hydrate. The temperature of the liquid bath was maintained at 270 K.

of CO<sub>2</sub> hydrate. Generally, the internal pressure in the cell decreased exponentially, while the internal temperature increased due to hydrate formation. There was also a decrease as  $\Delta P$  approached the temperature of the liquid bath. When the  $\Delta P$  was greater than 1 MPa and the formation

time was smaller than five hours, the internal pressure rapidly decreased at the last stage of formation time and then reached a state of equilibrium (Fig. 2). This tendency was often observed in the case of CO<sub>2</sub> and partly in the case of mixed gas.

Fig. 3 shows the relationship between formation time and  $\Delta P$ . The formation time was almost in the range of 1-10 hours and seemed to have no dependence on both  $\Delta P$  or the mixing ratio of gases (Fig. 3a). Besides, the formation time was less than one hour when the temperature was relatively high (Fig. 3b). The formation time of CH<sub>4</sub> hydrate was highly variable and sometimes reached about hundred hours, whereas that of CO<sub>2</sub> hydrate was small even during conditions of high  $\Delta P$ . These results indicate that the formation speed of hydrate from ice and gas is not determined by  $\Delta P$  only, although weak temperature effects were observed and formation of CO<sub>2</sub> hydrate was relatively compared with that of CH<sub>4</sub> hydrate.

**Formation and dissociation process of hydrate based on equilibrium conditions**

After the guest gas was instantaneously discharged or recharged from the equilibrium condition, the internal temperature and pressure changed and approached the original values, respectively. Six examples (three formation and three dissociation processes of CO<sub>2</sub> hydrate) of the

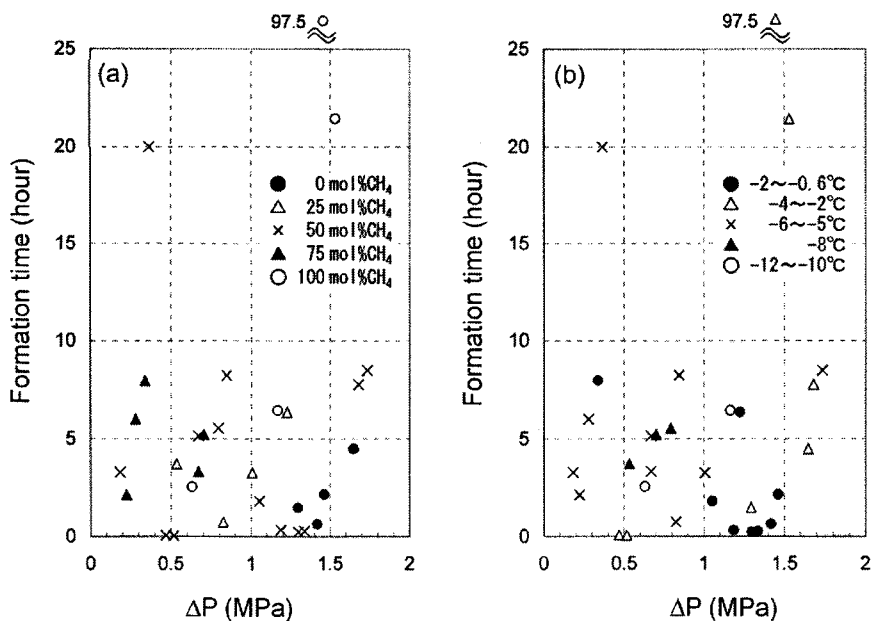


Fig. 3. Formation time of CH<sub>4</sub>, CO<sub>2</sub> and their mixed-gas hydrate plotted against  $\Delta P$ . (a) Parameter: mole fraction of CH<sub>4</sub>, 0 mol%CH<sub>4</sub> means 100 mol%CO<sub>2</sub>, (b) parameter: temperature of the liquid bath.

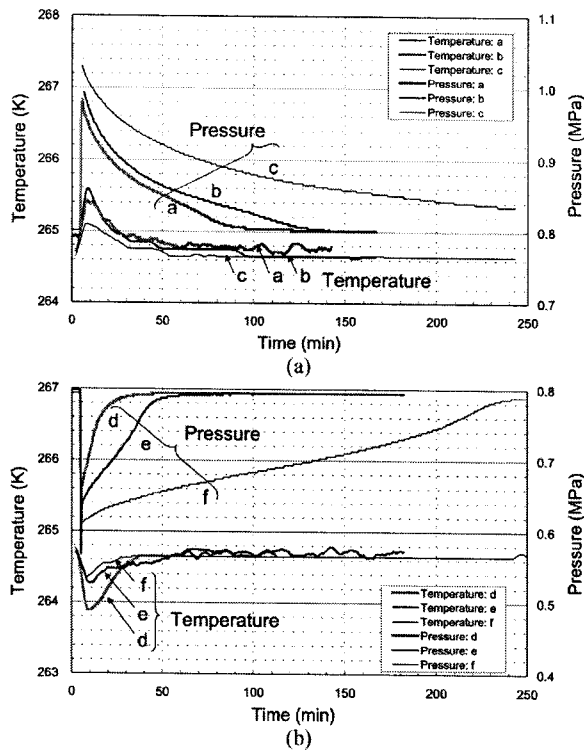


Fig. 4. Time variations of internal temperature and pressure during the formation and dissociation of  $\text{CO}_2$  hydrate. (a) Three cases of hydrate formation. (b) Three cases of hydrate dissociation.

time variations in temperature and pressure were plotted in Fig. 4. Initial temperature and pressure of their runs were 264.7 K and 0.80 MPa, respectively. Formation and dissociation speeds were different in each case, while the initial pressure changes were almost the same value of 0.2 MPa. Since the internal temperature varied largely in the interval of rapid change in pressure, we infer from this that latent heat release or absorption mainly caused temperature changes. As seen in Fig. 2, the internal pressure rapidly decreased at the last stage of hydrate formation (a and b in Fig. 4). Further investigation is required to determine why the formation speed of  $\text{CO}_2$  hydrates increase at the last stage.

On the other hand, when the gas was discharged and the pressure value of 0.2 MPa was established under conditions of equilibrium, the dissociation of hydrate began and the speeds of dissociation were very fast at the first stage within a minute and after that the speeds were reduced. These two stages in the dissociation process were also observed by Ebinuma *et al.* (2002). Furthermore, it was often observed that dissociation speed rapidly increased at the last stage

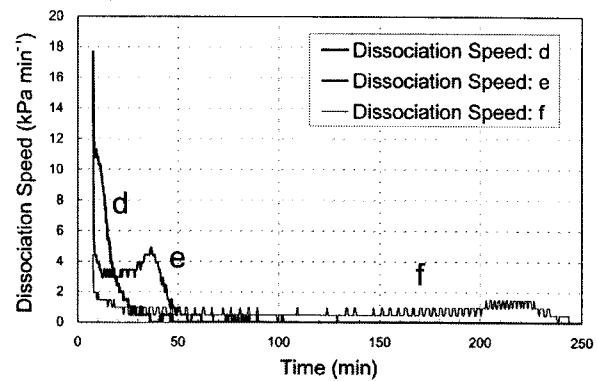


Fig. 5. Time variations of dissociation speed in three particular cases (d - f) in Fig. 4.

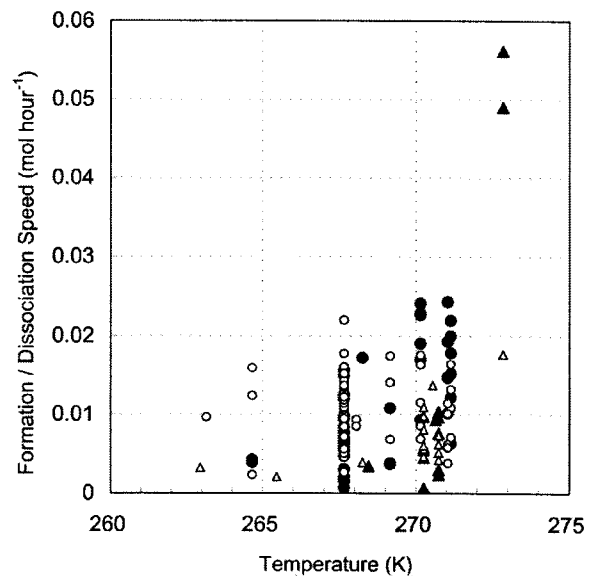


Fig. 6. Formation and dissociation speeds plotted against temperature. ●: formation speed of  $\text{CO}_2$  hydrate, ○: dissociation speed of  $\text{CO}_2$  hydrate, ▲: formation speed of  $\text{CH}_4$  hydrate, △: dissociation speed of  $\text{CH}_4$  hydrate.

of dissociation (e and f in Fig. 4). Fig. 5 shows the time variation of dissociation speed and it is obvious that small peaks were observed at 37 min in the case of e and at 203-227 min in the case of f. These results indicate that a self-preservation effect, first reported by Handa (1986) and investigated by Yakshev and Istomin (1992), may affect the middle stage of dissociation and limit the speed of hydrate dissociation.

Formation and dissociation speeds of  $\text{CH}_4$  and  $\text{CO}_2$  hydrates were obtained from the amount of consuming/releasing gas divided by formation/dissociation time, respectively. They are plotted with respect to temperature in

Fig. 6. Since the initial  $\Delta P$  was established at 1.5 MPa and a certain amount of gas hydrate samples had already formed, initial hydrate density before discharging or recharging gas from the equilibrium condition seemed to be almost the same and was estimated to be at a volume of about 22%.  $\Delta P$  as a pressure change for discharging or recharging gas was observed to be within the range of 0.05-0.56 MPa in Fig. 6. Formation and dissociation speeds of  $\text{CH}_4$  hydrate at 272.9 K, where the four phases of hydrate, ice, liquid water and gas coexist as a quadruple point, which was relatively high. Komai *et al.* (2002) obtained similar results to those of  $\text{CO}_2$  hydrate, which formed rapidly at 272 K, whereas it formed slowly below 269 K.

The data was sorted by  $\Delta P$  within a range of  $0.2 \pm 0.03$  MPa and formation/dissociation speeds are plotted against temperature in Fig. 7. Because change of hydrate density is estimated to be less than  $4 \pm 0.6$  vol% when  $\Delta P$  is  $0.2 \pm 0.03$  MPa, we may say that we can discuss the temperature effect on formation/dissociation speed under nearly the same conditions. It is clear that formation and dissociation speeds of  $\text{CO}_2$  hydrate are higher than those of  $\text{CH}_4$  hydrate. It is possible that a quasi-liquid layer or a liquid film on the ice surface effects the formation process of gas hydrate because  $\text{CO}_2$  is more dissolvable in water than  $\text{CH}_4$ . Fig. 7 also shows that these speeds do not have a

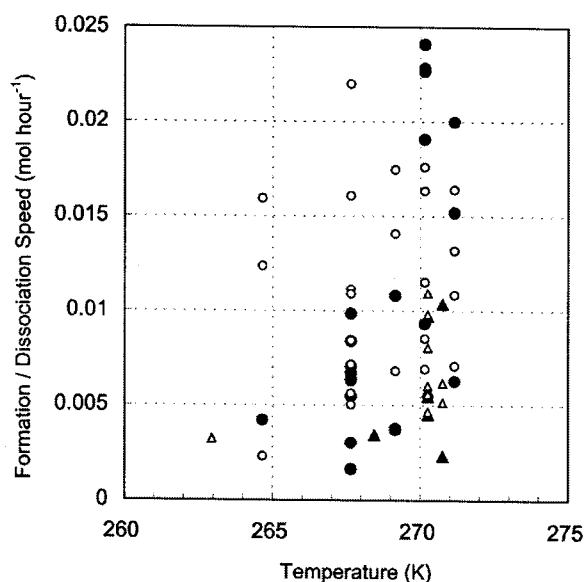


Fig. 7. Formation and dissociation speeds plotted against temperature.  $\Delta P$  is limited within a range of  $0.2 \pm 0.03$  MPa. ●: formation speed of  $\text{CO}_2$  hydrate, ○: dissociation speed of  $\text{CO}_2$  hydrate, ▲: formation speed of  $\text{CH}_4$  hydrate, △: dissociation speed of  $\text{CH}_4$  hydrate.

clear correlation with temperature. This implies that although temperature must be one of the factors in controlling the formation and dissociation speeds, other factors affect speeds as well.

Fig. 8 shows the relationship between formation and dissociation times and  $\Delta P$ . The internal pressure of the cell was changed within 0.05-0.6 MPa. Under  $\Delta P$  less than 0.1 MPa, which corresponds to about 1.5 K for  $\text{CH}_4$  hydrate and about 3 K for  $\text{CO}_2$  hydrate and the degree measured for supercooling formation and dissociation times were less than 30 minutes. On the other hand, the formation and dissociation time increased according to the  $\Delta P$  and their dispersion also increased substantially. In Fig. 8, we found that there was little difference between  $\text{CH}_4$  and  $\text{CO}_2$ , and that the formation and dissociation time cannot be decided only by  $\Delta P$ .

#### Formation and dissociation process of hydrate under conditions of equilibrium

Equilibrium pressure is plotted against initial pressure in the case of mixed gas ( $\text{CH}_4$  and  $\text{CO}_2$ ) hydrate in Fig. 9. The ratio of mixed gas initially charged was 50 mol% $\text{CH}_4$ . It is clear that the equilibrium pressure increased in accordance with the initial pressure. When the mixed-gas

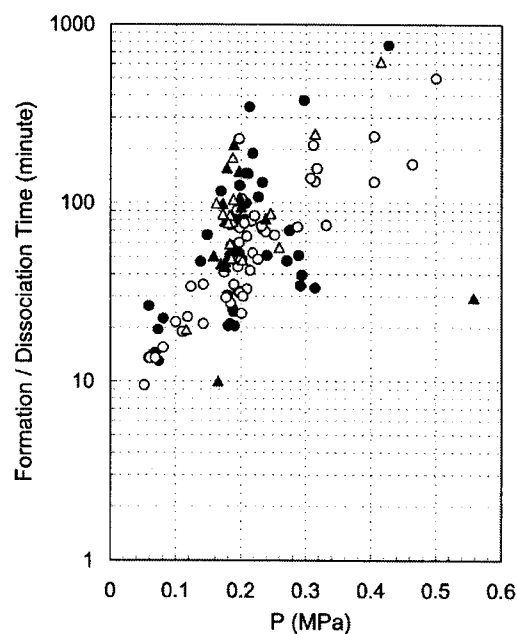


Fig. 8. Formation and dissociation times plotted against  $\Delta P$ . ●: formation time of  $\text{CO}_2$  hydrate, ○: dissociation time of  $\text{CO}_2$  hydrate, ▲: formation time of  $\text{CH}_4$  hydrate, △: dissociation time of  $\text{CH}_4$  hydrate.

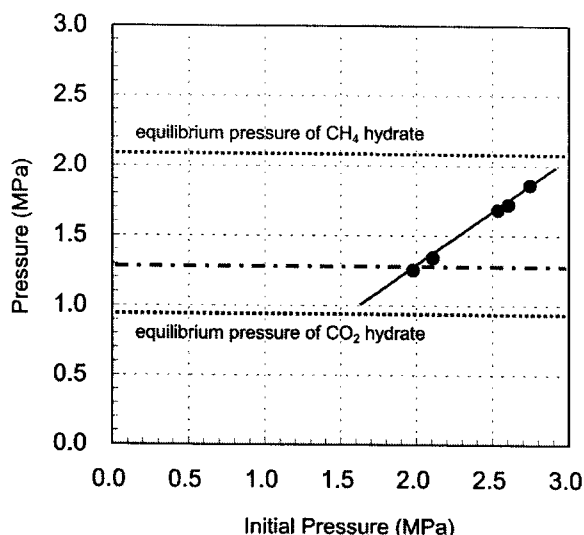


Fig. 9. Relation between the equilibrium pressure of mixed-gas ( $\text{CH}_4$  and  $\text{CO}_2$ ) hydrate and the initial pressure at the formative stage. The initial ratio of the mixed gas was 50 mol% $\text{CH}_4$ . Dotted lines represent the equilibrium pressures of  $\text{CH}_4$  and  $\text{CO}_2$  hydrates at temperatures of 268 K, respectively. Dashed line means an equilibrium pressure of mixed-gas hydrate obtained using the CSM-HYD Hydrate Program (Sloan 1998) when the mixing ratio of the gas phase is 50 mol% $\text{CH}_4$ .

hydrate forms from gas and ice in a finite and closed system, the concentration of  $\text{CH}_4$  in the gas phase increases because  $\text{CO}_2$  concentrates in the hydrate phase. The anticipated equilibrium pressure of 1.281 MPa for  $\text{CO}_2$  hydrate was obtained from a CSMHYD Hydrate Program (Sloan 1998) with the mixing ratio of the gas phase of 50 mol% $\text{CH}_4$  (dashed line in Fig. 9). Because the equilibrium pressures obtained in this experiment were larger than the anticipated value, the concentration of  $\text{CH}_4$  in the gas phase seems to be larger than 50 mol% $\text{CH}_4$ .

If the initial pressure is high, a degree of supercooling that corresponds to the driving force for hydrate crystallization increases. The difference in the driving forces for hydrate crystallization between  $\text{CH}_4$  and  $\text{CO}_2$  hydrates also becomes relatively small. The concentration of  $\text{CH}_4$  in the hydrate phase increases, hence the equilibrium pressure becomes relatively high. On the contrary, if the initial pressure is low,  $\text{CO}_2$  molecules are more fixed in hydrate cages than is the case for  $\text{CH}_4$  molecules and the equilibrium pressure becomes relatively low. Such fractionation in the formation of mixed-gas hydrate is similar to the kinetic isotope effect in isotopic mass fractionation for snow (Hachikubo et al. 2000).

Suppose that  $\text{CH}_4$  and  $\text{CO}_2$  are independent of each other in the process of hydrate formation. In such a case, the equilibrium pressure of 50 mol% $\text{CH}_4$  mixed-gas hydrates would consist of a middle value between the equilibrium pressures of  $\text{CH}_4$  and  $\text{CO}_2$  hydrates. However, substantial data of the equilibrium pressure in Fig. 9 exceeds the middle value, so that it requires further experiments and consideration on the kinetics of how mixed gas molecules are fixed in hydrate.

#### 4. Conclusion

Formation process of  $\text{CH}_4$ ,  $\text{CO}_2$  and their mixed-gas hydrates from fine ice powder and the dissociation process of  $\text{CH}_4$  and  $\text{CO}_2$  hydrates are investigated by monitoring temperature and pressure conditions in a pressure cell. Although this study does not quantitatively illuminate the factors for controlling the phase transition of gas hydrate, the results suggested that the formation and dissociation speed of gas hydrate is not controlled only by temperature and  $\Delta P$  alone. We need further studies about the existence of the quasi-liquid layer on the ice surface in the formation process and the self-preservation effect in the dissociation process.

In this study, we suggest that initial pressure at the formation of mixed-gas hydrate determines its own equilibrium pressure. In future work, the composition of each gas both in gas and hydrate phases will be analyzed directly by gas chromatography, with which the fractionation model will be developed to understand the equilibrium state of mixed-gas hydrate.

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