

Equilibrium Properties and Kinetics of Methane and Carbon Dioxide Gas Hydrate Formation/Dissociation

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INTRODUCTION

Large quantities of gas hydrates, clathrate compounds of water and gases formed under high pressure and low temperature, are found in marine sediments and in cold regions. To produce large amount of methane gas from the reservoir with a reasonable way, it is necessary to obtain fundamentals on the mechanism of formation and dissociation and the properties under the practical situations, including phase equilibria and kinetics of gas hydrates. In addition, we have proposed the displacing method of gas hydrates, so that methane gas is extracted from the reservoir by displacing methane with carbon dioxide in molecular level. The main purposes of this research are to acquire the further understanding for the mechanism of hydrate formation/dissociation, and also to accumulate engineering data for completing the original concept of displacing method. We have carried out an experiment on the formation and dissociation of methane and carbon dioxide, using an apparatus consisting of extremely high pressure vessel and observation windows. This paper presents the experimental results on the properties of gas hydrates formation and dissociation under the condition of three phase equilibrium, and some discussion on kinetics and the mechanism of gas hydrate formation.

EXPERIMENTAL

The experimental apparatus, in which the formation and dissociation of gas hydrate could be observed, was designed and manufactured, so that the several conditions of pressure, temperature and concentration of gases could be precisely controlled. Fig.1 illustrates the schematic diagram of the apparatus and the measuring system of the experiment. The pressure cell (1), made of stainless steel and with 90 ml in internal volume, can be used under the pressure condition of up to 40 MPa. It contains three glass windows (2) for observation, a magnetic type mixing equipment (3), and some nozzles (4) for introducing gas and liquid component. The pressure cell is installed within a constant temperature bath (5) filled with cooling agent of ethylene glycol, where the temperature can be controlled with the accuracy of ± 0.2 °C. Gas and liquid fluids are introduced into the cell using a high pressure pump (6) and a fluid supplier system (7), and then are adjusted so that the pressure would be kept constant or free to change by means of two cylinder type controllers (8). The accuracy of controlled pressure is designed to be ± 0.05 MPa. Four transducer for detecting and controlling the pressures are equipped, and five thermocouples are installed for measuring the temperatures inside the cell as shown in Fig.1. The observation system including a optical fiber borescope (9) and a CCD camera (10) can be utilized for this apparatus.

The procedure of the experiment on the three phase equilibrium of gas hydrate are described in the following. First, a quantity of pure water is supplied by the high pressure pump into the pressure cell, and other portion of the volume is filled with pressurized gas component by the fluid supplier system. The quantities can be calculated as equivalent volume portions needed for hydrate structure. The internal pressure can be adjusted, using both the cylinder units in liquid phase and the supplier system in gas phase. The formation of gas hydrate is observed during the temperature of whole system going down, while the pressure is no longer controlled at this situation. The accumulation of hydrate would complete for about a couple of hours, after which the temperature is controlled to go up with the constant rate for getting the equilibrium data of dissociation. The optical cell and the spectrometric system are equipped at the glass window for detecting the nucleation and the change of liquid phase structure. A lot of experimental data, such as temperatures, pressures and gas concentrations, and other experimental conditions, are measured and analyzed using the data acquisition system.

RESULTS AND DISCUSSION

The solubility of gases and gas transport into liquid phase are important factors to promote the formation of gas hydrates in the three phase equilibrium condition. In this experiment, two types of mixing and bubbling operations were adopted for the promotion of nucleation. Fig.2 shows photographic figures for the formation of methane hydrate, observed through the glass window. These results were obtained under the same condition as the pressure was approximately 10 MPa and the temperature was 4.0 to 6.0 °C. As shown in the left figure, a lot of fine fragments of

methane hydrate were formed around the mixing blade and were accumulated in the liquid phase. On the contrary, as shown in the right figure, a lot of gas bubbles from the nozzle turned into solid phase droplets of methane hydrate at the interface of gas and liquid phase. The following experimental results are mainly related to the mixing operation, because it enables the equilibrium properties to become more favorable and reproductive. For keeping sufficient saturation or dissolved condition of gases into liquid phase, each experiment requires previous mixing operation for 30 minutes and enough mixing speed of no lower than 170 rpm.

Plenty of experiments using the gas hydrate formation apparatus have been conducted under the conditions, such as gas component, initial pressure and temperature, and restating hysteresis situation. Fig.3 shows the trend curves for temperature and pressure, obtained using the gas component of CH_4 (100%). TEMP1 represents the temperature measured by No.1 thermocouple at the center of the cell, and TEMP2 the controlled one outside the cell. PRES means the pressure of liquid phase inside the cell. This figure shows that the formation of gas hydrates eventually started during the process of temperature decreasing, because slight increases of temperature appeared after the nucleation point due to the heat of formation. The rapid decrease of pressure was observed around the formation point, while the pressure gradually decreased as the temperature became lower due to the change of solubility. On the other hand, the dissociation of gas hydrate was observed during the process of temperature increasing, from which the increase of temperature started to decline. Fig.4 shows the trend curve of differential temperature measured by No.1 and No.5 thermocouples as a heat balance in the experiment. The first peak on the curve indicates the exothermic heat of formation, and the last one the endothermic heat of dissociation. According to these relations and the observation, critical temperatures and pressures necessary for gas hydrate formation and dissociation can be determined as in Table 1. These results include the properties for the three phase equilibrium. Compared with data in experiments No.4 and No.9 for CO_2 and CH_4 hydrate, the critical temperatures of CH_4 hydrate formation and dissociation are much higher than those of CO_2 hydrate. Further, it is found that the critical temperatures of formation and dissociation increase as the initial pressures become higher in both cases of CO_2 and CH_4 hydrates.

Fig.5 shows the three phase equilibrium relation obtained through the series of experiment for CO_2 and CH_4 hydrate. Upper two lines are the formation and dissociation equilibrium curves for CH_4 gas hydrate, the relation between critical temperatures T and pressures P, and lower lines for CO_2 gas hydrate. In other words, gas hydrate can be present as solid phase with gas and liquid components at higher position from curves for formation, and it no longer exists at lower position from curves for dissociation. From the results it is clear that the relation between P and T is approximately linear in semi-log plotting, and that the critical pressures of CH_4 are relatively higher than those of CO_2 assuming the same temperature condition. This suggests that the formation of CH_4 hydrate requires much higher potential or activation energy rather than in the case of CO_2 hydrate. In addition, it is found that the equilibrium curves for the formation of hydrates are placed at upper position compared with those for the dissociation. Further, the equilibrium data measured in case of dissociation agree well with estimated values using theoretical methods of kinetics, but those in case of formation largely differ from the theoretical values. These large differences may include interesting phenomena and fundamentals on the mechanism of gas hydrate formation. Thus, further experiments were carried out on the behavior of history and hysteresis observed the process of formation and dissociation of gas hydrates.

Fig.6 illustrates the history curve of P and T obtained in the experiment No.39 for CH_4 hydrate. The formation process proceeds on the oscillated curve between A and D, and the dissociation process on the curve between E and F. The differences of temperature and pressure between formation and dissociation equilibria are approximately 3.5 °C and 0.5 MPa, respectively. The history of P and T is usually regarded to be the super cooling effect in the process of formation. The temperature differences obtained by the experiment using CO_2 were quite smaller than that in case of CH_4 . In addition, the super cooling effect clearly appeared in the case that the gas component was introduced by the way of bubbling. These results suggest that the super cooling effect in the history behavior might be largely related to the interface conditions, the way of gas introduction, and the component of gas and liquid.

Fig.7 shows the hysteresis curves for demonstrating the effect of restarting situations, obtained by continuous three experimental runs in the same conditions. The second and third runs were restarted immediately after completing the previous run. In the first run of experiment, the temperature of initiating formation was 15.2 °C at the pressure of 17.5 MPa. However, the formation temperature was shifted to 16.6 °C in the second run, and up to 16.8 °C in the third run. This means that the formation temperatures increase in case of restarting situations, so that they approach the dissociation temperatures or the theoretical temperature for three phase equilibrium. Another experimental run showed that the formation temperature of second run shifted by 2.5 to 3 °C compared with that of the first run, but that of third run recovered to the level of first run if the liquid with dissolved gas was left as the final condition of second run for 12 hours. These results

may suggest that the hysteresis behavior for gas hydrate formation largely depends on the presence of cluster structure in liquid phase, the promotion process of nucleation, and the saturation or dissolved condition of gases into liquid phase.

CONCLUSIONS

Experimental studies on the properties of three phase equilibrium and the process of formation and dissociation of gas hydrates have been carried out, using the specially designed experimental apparatus. As a result, it was found that measured equilibrium data in case of dissociation agree well with estimated values using theoretical methods, but those in case of formation largely depend on the interface conditions, the way of gas introduction, the structure of liquid phase, and the history and hysteresis process of hydrate formation. Thermodynamics properties of gas hydrates were also discussed on the basis of temperature and pressure data in formation and dissociation of gas hydrate. In order to make clear the effects of liquid structure and interface condition on the detail process of formation of gas hydrates, further experimental and theoretical approaches are necessary on the mechanism of nucleation and cluster structure.

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REFERENCES

- Burrus, R.C.: Crystallization of Natural Gas Hydrate: Video Microscopy and Mass Balance on Nucleation and Growth, Proc. Conf. Drilling Hydrates in Offshore, Japan, 182, (1995)
 Holder, G.D., Zett, S.P. and Pradhan, N.: Phase Behavior in Systems Containing Clathrate Hydrates: A Review, Reviews in Chemical Engineering, 5, 1-70, (1988)
 Uchida, T., Hondoh, T. and Mae, S.: Effects of Temperature and Pressure on the Transformation Rate from Air Bubbles to Hydrate Crystals, Ann. Glaciol., 20, 143-147, (1994)
 Matsumoto, R.: Feasibility of Methane Hydrate under the Sea as a Natural Gas Resource, J. Jap. Assoc. Petro. Tech., 60(2), 147-156, (1995)

Table 1 Experimental results of the formation and dissociation equilibrium data.

Exp.No.	Initial Pressure (MPa)	Formation Equilibrium		Dissociation Equilibrium			
		Pressure (MPa)	Temperature (°C)	Pressure (MPa)	Temperature (°C)		
EXMH09	5.80	5.4	4.4	4.2	5.0	CH ₄	
EXMH08	8.05	7.1	5.8	6.8	10.6		
EXMH24	10.20	9.4	8.1	8.6	11.7		
EXMH11	10.50	9.7	8.8	8.6	12.0		
EXMH07	11.90	10.8	8.8	9.9	13.2		
EXMH06	13.38	12.5	11.0	11.6	14.1		
EXMH29	17.97	17.0	12.9	16.8	17.1		
EXMH30	20.00	18.8	14.2	18.6	18.0		
EXMH12	3.1	2.4	4.0	1.9	5.0		CO ₂
EXMH13	4.0	3.4	6.0	2.6	6.9		
EXMH04	4.9	4.2	9.4	4.1	9.9		

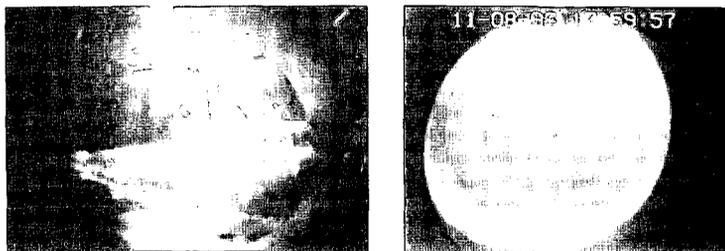


Fig.2 The observation of methane gas hydrate formation.

(Left figure) In case of mixing operation. (Right figure) In case of bubbling operation.

P=10.0 MPa, T=8.0 °C

P=10.0 MPa, T=4.0 °C

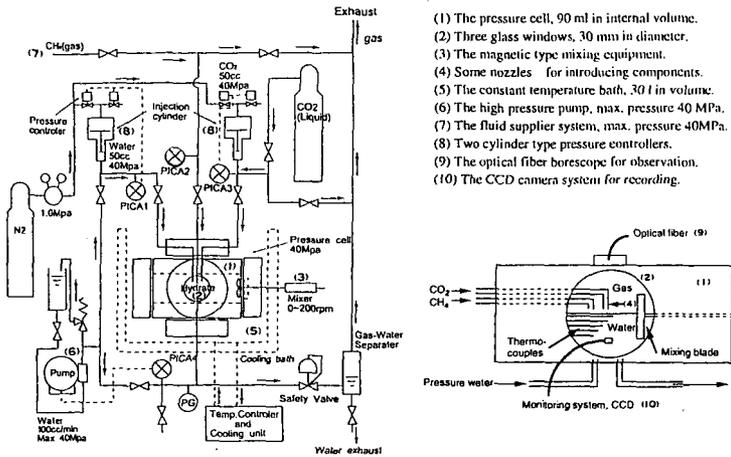


Fig.1 The schematic diagram of the experimental apparatus and the measuring system. (Upper figure) Main system. (Lower figure) Pressure cell and measuring sensors.

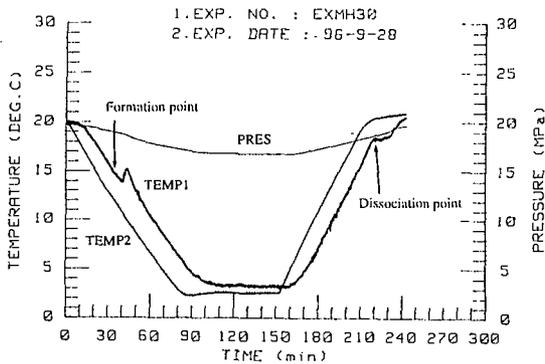


Fig.3 The trend curves of pressure and temperature obtained in the experiment for methane gas hydrate formation and dissociation.

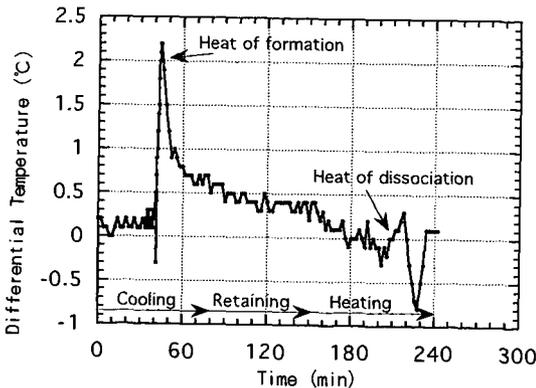


Fig.4 The change in differential temperature, and heat valance of gas hydrate formation and dissociation.

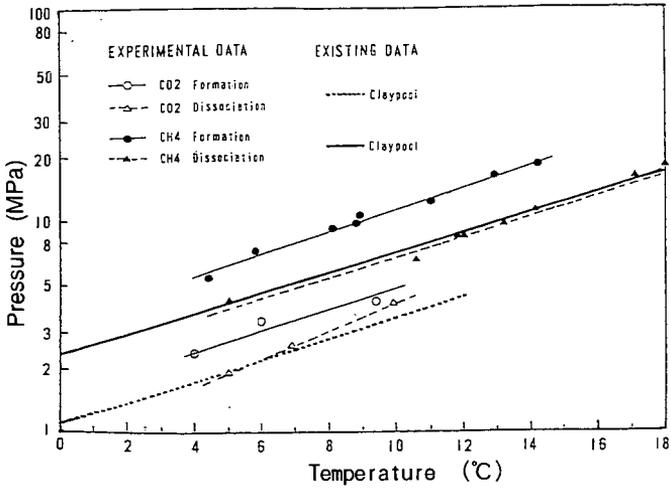


Fig.5 The relations between pressure and temperature in three phase equilibrium condition for CO₂ and CH₄ gas hydrates.

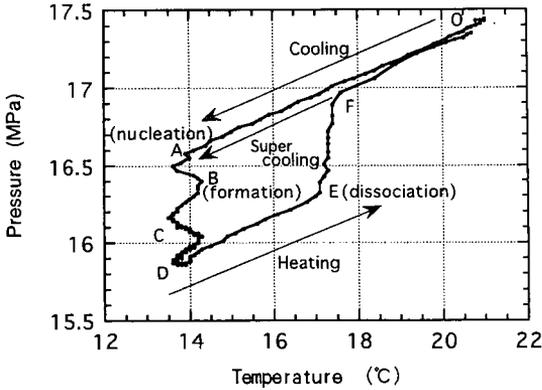


Fig.6 The history curve of pressure and temperature in the process of gas hydrate formation and dissociation.

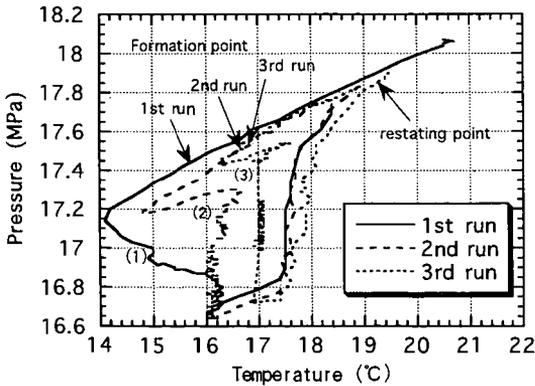


Fig.7 The hysteresis curves of pressure and temperature in the process of gas hydrate formation and dissociation.