

Phase and kinetic behavior of the mixed methane and carbon dioxide hydrates

Youngjune Park, Jaehyoung Lee*, Kyuchul Shin, Jiwoong Seol, Kyung-Min Lee, Dae-Gee Huh*,
Keun-Pil Park* and Huen Lee†

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea

*Korea Institute of Geoscience and Mineral Resources, 30 Gajeong-dong, Yuseong-gu, Daejeon 305-350, Korea
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Abstract—Large amounts of CH₄ are stored as hydrates on continental margins and permafrost regions. If the CH₄ hydrates could be converted into CO₂ hydrate, they would serve double duty as CH₄ sources and CO₂ storage sites in the deep ocean sediments. As preliminary investigations, both the phase behavior of CH₄ hydrates and kinetic behavior of CO₂ hydrate were measured at versatile conditions that can simulate actual marine sediments. When measuring three-phase equilibria (H-L_v-V) containing CH₄ hydrate, we also closely examined pore and electrolyte effects of clay and NaCl on hydrate formation. These two effects inhibited hydrate nucleation and thus made the hydrate equilibrium line shift to a higher pressure region. In addition, the kinetic data of CO₂ hydrate in the mixtures containing clay and NaCl were determined at 2.0 MPa and 274.15 K. Clay mineral accelerated an initial formation rate of CO₂ hydrate by inducing nucleation as initiator, but total amount of formed CO₂, of course, decreased due to the capillary effect of clay pores. Also, the addition of NaCl in sample mixtures made both initial formation rate and total amount of CO₂ consumption decrease.

Key words: Natural Gas Hydrate, Clathrate Hydrate, Methane, Carbon Dioxide, Clay, NaCl

INTRODUCTION

Under specific conditions, generally low temperature and high pressure, when water molecules are reacted with low molecular weight gases such as methane, ethane, nitrogen, carbon dioxide, etc., non-stoichiometric crystalline structures, namely clathrate hydrate - commonly called the gas hydrate - can be formed [Sloan, 1998]. Water molecules (host) are connected by hydrogen bonds and form the different shapes of cages where the gas molecules (guest) are stably located. Gas hydrates are divided into three distinct crystal structures. Each structure is composed of different shape and size of cages. The structure I (sI) gas hydrate has two 5¹²(D) cages and six 5¹²6²(T) cages, and structure II (sII) has sixteen 5¹²(D) cages and eight 5¹²6⁴(H) cages in a unit cell. Unlike sI and sII gas hydrates which have cubic structures, structure H (sH) gas hydrate is a hexagonal structure which consists of three 5¹²(D), two 4³5⁶6³(D) and one 5¹²6⁸(I) cages [Jefrey, 1984].

On the continental margins and in permafrost regions, vast hydrocarbon resources exist in hydrate form [Makogon, 1988; Kim et al., 2005]. It has been reported that world hydrate reserves are estimated at about 10¹⁶ m³ and the enormous amount of natural gas captured in hydrate represents an estimated 53% of all fossil fuel reserves on earth [Kvenvolden, 1994]. By reason of its vast quantities, many researchers have suggested the potential application of natural gas hydrate to premium fuel for this century [Ridley and Dominic, 1988; Sloan, 2003]. At the same time, it has been proposed that CO₂, one of the well-known global warming gases, possibly could be stored in the ocean floor as a CO₂ hydrate [Brewer et al., 1997]. More-

over, the replacement of CH₄ with CO₂ in the hydrate might be suggested as a promising method for recovering CH₄ from natural gas hydrate deposited on the ocean floor. The dual mechanisms occurring during the swapping process between CO₂ and CH₄ in gas hydrate deposits was closely examined by identifying cage occupancy [Lee et al., 2003]. Microscopically, the global warming gas (CO₂) is injected and diffused into gas hydrate deposits and eventually competes with CH₄ for the better occupancy to large cages. In the case that CO₂ molecules have sufficient enclathration ability, then the already existing CH₄ molecules have to be pulled out and recovered for the desired energy source. Thus, two big tasks of CO₂ storage and CH₄ recovery proceed in a spontaneous way at the same time. However, for a better understanding of the proposed dual behavior, the basic information on phase equilibria and formation kinetics of CH₄ and CO₂ hydrates needs to be first secured, particularly for developing real process technology. Additionally, the pore and electrolyte effects caused by marine sediments and salts have to be carefully examined to simulate the real conditions occurring in the ocean floor. Previously, Handa and Stupin [1992] studied porous medium effects on gas hydrate formation and found that the equilibrium pressures of CH₄ and C₃H₈ hydrates in silica gel were shifted to the higher pressure region compared to those of the bulk hydrates. Seo et al. [2002] reported the hydrate phase equilibria for the binary CH₄+water and CO₂+water mixtures in varisized silica gel pores. Electrolyte and clay effects on phase and kinetic behavior of CO₂ hydrates are reported by Lee et al. [2002a]. For more fundamental information we investigated the formation kinetics of CO₂ hydrates [Chun et al., 1996] in various concentrations of NaCl and clay mineral at 2.0 MPa, 274.15 K together with the phase equilibrium measurements of CH₄ hydrates in the confined and salt-containing surroundings.

†To whom correspondence should be addressed.
E-mail: h_lee@kaist.ac.kr

Table 1. Average value of pore size, surface area and volume

| Average pore size (Å) | Average surface area of pores (m ² /g) | Average volume of pores (cm ³ /g) |
|-----------------------|---|--|
| 90.3315 | 35.1711 | 0.079426 |

EXPERIMENTAL SECTION

1. Phase Equilibria of CH₄ Hydrate in the Deep Ocean Sediments

CH₄ used in the current study was purchased from the Gosok Gas Co., Korea and had a stated purity of 99.99 mol%. NaCl was supplied from Aldrich Chemical Company, Inc, USA and had a stated purity of 99+%. All chemicals were used without further purification. De-ionized water was purchased from Merck Chemical Co., Germany. Clay was Na-Montmorillonite (purchased by Crook County, Wyoming, USA) and its goods name is SWy-2. Size distribution of clay mineral is listed in Table 1. The sample with low clay-content (25 wt%) was prepared by dispersing clay in water with a magnetic stirrer for 6 to 8 hours, and the other with high clay-content (77 wt%) was prepared by absorbing in the evacuated desiccator for more than 3 days. A schematic diagram of the experimental apparatus is shown in Fig. 1. The whole system was constructed to measure the dissociation pressures and temperatures of specified hydrates, and also to measure the volumetric consumption gas rate during hydrate formation. Approximately 25 cm³ of the aqueous solution containing clay or NaCl was charged into the high pressure cell (made of 316-stainless-steel and its internal volume was about 150 cm³) in the water-ethylene glycol mixture bath controlled by circulator (Jeio Tech Co., MC-31, Korea). The air in the cell was eliminated with flushing several times. The pressure of system was initially supplied from a gas cylinder and reached desired pressure by a micro flow syringe pump (ISCO Co., 260D, USA) and the temperature kept constant as a temperature just above that at which gas hydrate was formed. The pressure in the cell was measured by a Heise pressure gauge (Dresser Instrument, CMM 104957, 0-60.0 MPa, USA), and the actual operating temperature was measured

by *in-situ* K-type thermocouple probe with a digital thermometer (Cole-Parmer, 8535-26, USA). Clathrate hydrate nucleation was then induced by agitation of a magnetic spin bar with immersed magnet in a bath. When gas hydrates were formed and the system pressure reached a steady state, the system temperature was increased at a rate of 1 to 2 K per hour to a condition at which the hydrate phase was dissociated and in coexistence with liquid and vapor phases. When a minute portion of crystals exists, the system temperature is kept constant at least for 8 to 10 hours. After the system pressure is stabilized, the pressure is considered as a hydrate dissociation pressure at that temperature [Bishnoi, 1996]. The existence of crystal could be confirmed by visual observation and pressure-temperature locus. However, in case of clay solution, it becomes almost impossible to directly observe the inner part of a cell. Instead, the dissociation equilibrium point was determined by examining the pressure-temperature trace with time.

2. Formation Kinetics of CO₂ Hydrate in the Deep Ocean Sediments

CO₂ used in the current study was purchased from the Gosok Gas Co., Korea and had a stated purity of 99.99 mol%. A schematic diagram of the experimental apparatus is also shown in Fig. 1. The experiment was carried out under isothermal temperature of 274.15 K and isobaric pressure of 2.0 MPa. The first experimental pressure was selected to a value below 0.5 MPa than the three-phase (H-L_v-V) equilibrium pressure at the experimental temperature, 274.15 K. The high pressure cell was filled with about 50 cm³ of de-gassed aqueous mixture. Four different cases were separately considered to see their independent effects on hydrate formation: pure water, clay emulsion, NaCl solution and NaCl solution containing clay. CO₂ gas was fed to the reactor and the mixture was stirred so as to be saturated with the feed gas. The pressure in the reactor was maintained at constant pressure of 2.0 MPa by using a syringe pump. The data acquisition system was used to obtain the flow rate signals by using a Mass flow meter (Brooks Instrument, 5850E, USA) and program (A PC-LabCard™, Advantech Co., Ltd, PCL711B, Taiwan) installed on a PC. By the stirring of the mixture again, the kinetic experiment of CO₂ hydrate formation commenced.

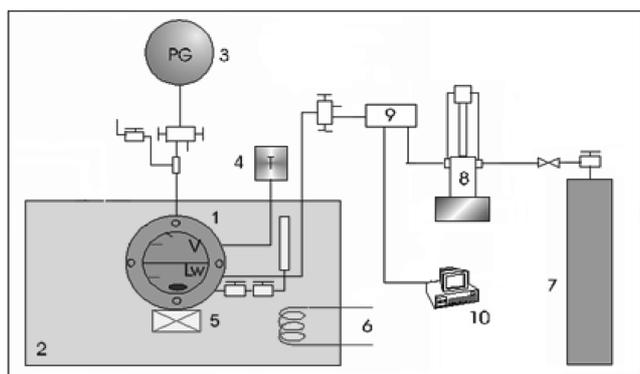


Fig. 1. Schematic diagram of experimental apparatus for equilibrium measurement and formation kinetics of gas hydrate.

- | | |
|---------------------|----------------------------|
| 1. Equilibrium cell | 6. External heat exchanger |
| 2. Water bath | 7. Gas cylinder |
| 3. Pressure gauge | 8. Syringe pump |
| 4. Thermocouple | 9. Flow meter |
| 5. Magnetic stirrer | 10. IBM computer |

RESULTS AND DISCUSSION

1. Phase Equilibria of CH₄ Hydrates in the Deep Ocean Sediments

We measured the equilibrium data of hydrate samples containing clay mineral and NaCl, and compared them with pure CH₄ hydrate data. In the mixture containing clay mineral, the solution itself becomes too opaque to determine the equilibrium point through visual observation. Therefore, one of the possible methods is to use the pressure-temperature locus with respect to formation/dissociation time. Fig. 2 shows the pressure-temperature (P-T) trajectory. The gas hydrate started to form directly after going through the three-phase equilibrium boundary, and rapid pressure drop occurred. With several equilibrium temperatures and pressures we obtained the complete equilibrium curves. The phase equilibria of CH₄ hydrate containing clay and NaCl were summarized in Fig. 3. As shown in Fig. 3, 25 wt% of clay did not affect hydrate equilibrium pattern to shift to either promotion or inhibition range. It must, however, be noted that water exists in bulk liquid phase when compared with those in

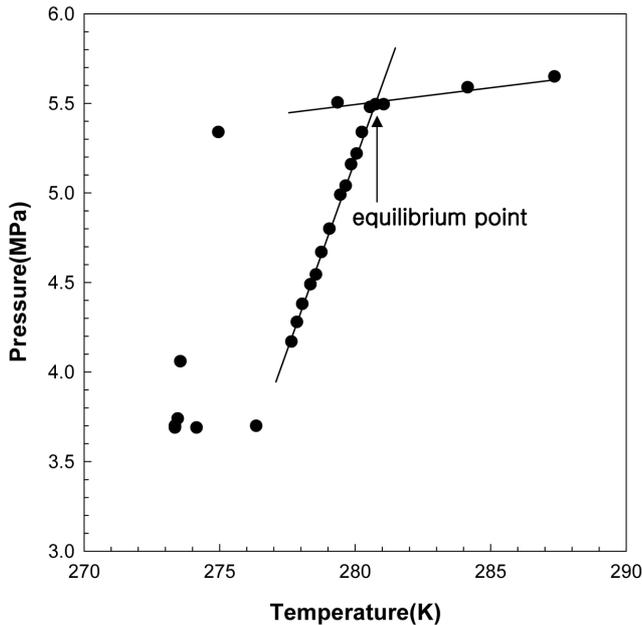


Fig. 2. Pressure-temperature trace during hydrate formation and dissociation process in $\text{CH}_4\text{-H}_2\text{O-clay-25 wt\%}$ system: Equilibrium pressure was 5.48 MPa at 280.55 K.

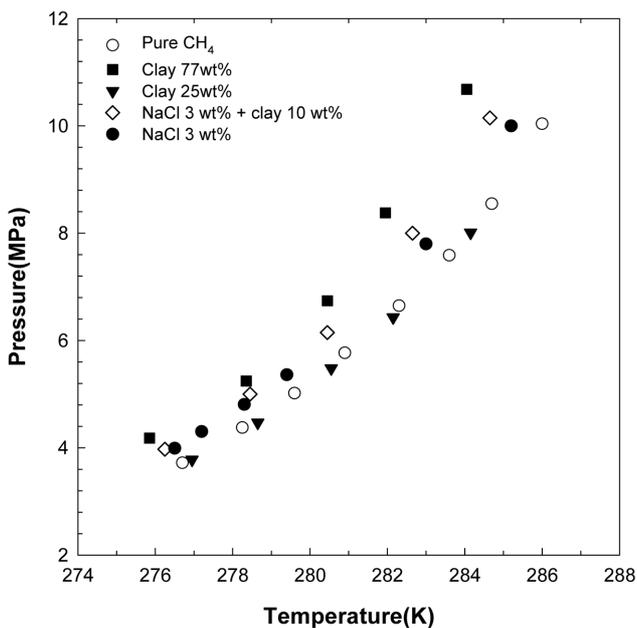


Fig. 3. Three phase (H- L_{II} -V) equilibrium condition of the $\text{CH}_4 + \text{H}_2\text{O} + \text{NaCl} + \text{clay}$ mixtures.

pores in clay mineral, and accordingly the formation phenomena of CH_4 hydrate occur dominantly in bulk liquid phase. Therefore, the resulting equilibrium curve coincided with the pure CH_4 hydrate equilibrium line. On the contrary, for 77 wt% clay mineral, there is no bulk water phase and water can only exist in the pores of clay. As can be expected, the equilibrium pressures of the mixture having high clay content appeared to be higher than those of pure CH_4 hydrate at a given temperature because of the capillary effect caused by clay mineral. This overall pattern indicates that the pores of clay

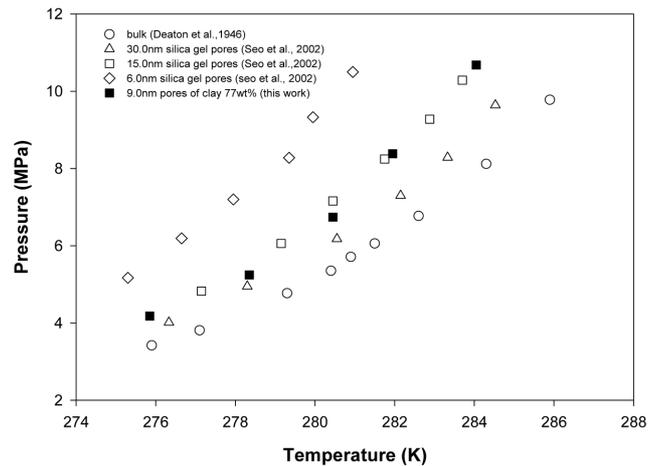


Fig. 4. Hydrate equilibria of the binary $\text{CH}_4 + \text{water}$ mixtures in various pore sizes.

inhibit hydrate formation.

NaCl was also added into the liquid water phase. Inhibition effects by NaCl have been well known in the hydrate field [Englezos, 1993]. As shown in Fig. 3, the equilibrium pressures of samples containing NaCl were found to be about 0.3 MPa, which is higher than those of the pure one. More importantly, we attempted to figure out the combined effects of clay and NaCl on hydrate formation. As mentioned earlier, the amount of 10 wt% clay was too small to affect the equilibrium pressure, and thus the equilibrium pressure of 3 wt% NaCl and 10 wt% clay content systems were prospected to be almost equal to those of 3 wt% NaCl added mixture without clay. However, the equilibrium lines of 3 wt% NaCl and 10 wt% clay samples were a little shifted to the left compared with those of 3 wt% NaCl solution. Accordingly, it seems to be clear that both clay and NaCl affect inhibition.

We also examined the pore size effects of clay on hydrate phase equilibrium using the varisized silica gels and the results are shown in Fig. 4. Seo et al. [2002] reported that the H(hydrate)- L_{II} (water)-V(vapor) lines in silica gel pores were shifted to a lower temperature and higher pressure region when compared with that of bulk hydrate. The decrease of pore size made the equilibrium line more shifted toward lower temperature at constant pressure. The experimental results showed that there was only a little difference between the phase equilibrium line of 15.0 nm silica gel pores and that of 9.0 nm clay mineral. It is known that a decrease of water activity leads to hydrate formation condition and the activity of water is related to the partial ordering and bonding of water molecules with hydrophilic pore surface. From the results of Fig. 4, we can suppose that the differences of structural and physical properties influenced water activity. Considering the differences of geometrical constraints and capillary effects between clay and silica gel, we can presume that the shifting tendency of the phase equilibrium line in silica gel pores follows a consistent pattern.

2. Formation Kinetics of CO_2 Hydrates in the Deep Ocean Sediments

The Formation kinetic data of CO_2 hydrates were obtained at 274.15 K and 2.0 MPa to simulate the deep ocean environmental conditions. Four different systems were attempted: pure water solu-

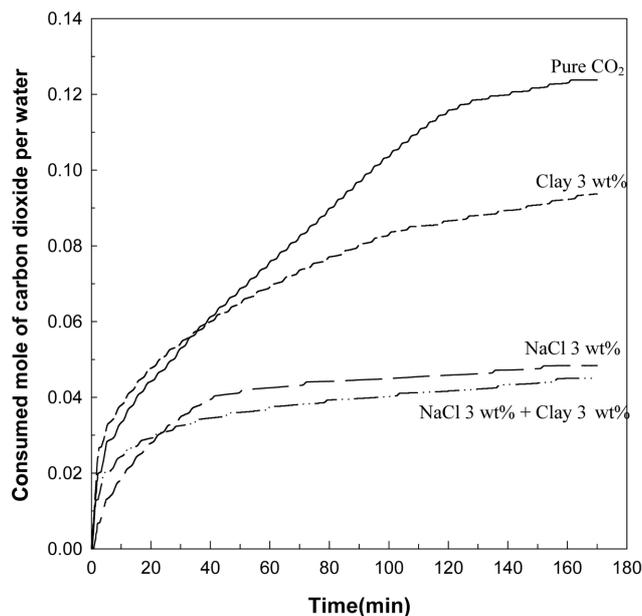


Fig. 5. CO₂ hydrate formation kinetics for mixtures containing clay and NaCl at 274.15 K and 2.0 MPa.

tion, 3 wt% clay added solution, 3 wt% NaCl solution, and a mixture including both 3 wt% clay and NaCl. The amount of consumed moles of CO₂ per 1 mole of water during hydrate formation was measured several times and obtained the converged values as presented in Fig. 5. For all the systems, CO₂ was rapidly consumed at the initial stage of hydrate formation and finally the conversion of water to hydrate was completed. For pure water solution hydrate the total consumed moles of CO₂ were about 0.1238 per mole of water, while for the solution containing 3 wt% of clay they were about 0.0937. It needs to be noted that the accumulated consumption of CO₂ was reduced when clay was added in the mixture. But, interestingly, the initial formation rate appeared to be a little higher than that of pure water. Similar inhibition behavior due to capillary effect shown in the case of CH₄ hydrates was also observed for CO₂ hydrates formed at the intermediate and final stages. However, at the initial stage, clay particles played a role in increasing the formation rate by inducing them as nucleation initiators. It needs to be noticed that the addition of clay did not affect the overall phase equilibrium pattern because water exists in excess around clay particles, and therefore the hydrate amount formed in the bulk water phase becomes much more dominant than that in the clay pores. For 3 wt% NaCl solution, the total consumption of CO₂ was 0.0484 moles per mole of water. The initial formation rate was found to be lower than that of the solution without NaCl. As also can be expected, for 3 wt% NaCl solution containing 3 wt% clay the final consumption of CO₂ was smaller than that of 3 wt% NaCl solution without clay, but its initial formation rate was higher because the accelerated nucleation was induced by clay particles. Our previous researches carried out at other pressure conditions also confirmed the same formation tendency [Lee and Lee, 2002b].

CONCLUSIONS

The ultimate goal of the present investigations is to establish the

conceptual process design for recovering CH₄ from CH₄ hydrate deposits and simultaneously sequestering CO₂. This dual mechanism occurring in a natural manner can provide considerable insight into resolving global warming and natural gas production. To accomplish the suggested huge target, both macro and micro approaches must be adopted and closely investigated by using highly sophisticated analytical instruments. However, as a preliminary study we focused on the phase equilibria of CH₄ hydrate and kinetic behavior of CO₂ hydrate for better understanding the swapping phenomenon occurring in real marine sediments. In this connection, the three-phase (H-L_H-V) equilibrium points of CH₄ hydrate system containing clay and NaCl were determined by pressure-temperature trace during hydrate formation and dissociation processes. At low clay concentrations the phase equilibrium line was not changed noticeably, but, at high concentration of clay, the inhibition of forming hydrate occurred because water penetrated clay interlayer pores and moreover hydrate formation occurred between layers. Clay-containing mixtures showed higher equilibrium pressures than those for the mixtures without clay at the same temperature condition, and this pressure discrepancy is considered to come from capillary effects of pores. Kinetic formation data of CO₂ hydrates in four different systems were obtained at 2.0 MPa and 274.15 K. Clay acts as a strong initiator that can accelerate initial formation rate. For the mixtures containing NaCl and clay together, the inhibition effects of both clay and NaCl on hydrate formation were also observed, which can be fully expected.

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REFERENCES

- Bishnoi, P. R. and Natarajan, V., "Formation and decomposition of gas hydrates," *Fluid Phase Equilibria*, **117**, 173 (1996)
- Brewer, P. G., Goyet, C. and Friederich, G., "Direct observation of the oceanic CO₂ increase revisited," *Proc. Natl. Acad. Sci. U.S.A.*, **94**, 8308 (1997).
- Chun, M.-K. and Lee, H., "Kinetics of formation of carbon dioxide clathrate hydrates," *Korean J. Chem. Eng.*, **13**, 620 (1996)
- Deaton, W. M. and Frost, E. M. Jr., *Gas hydrates and their relation to the operation of natural-gas pipe lines*, U.S. Bureau of Mines Monograph, 8 (1946).
- Englezos, P., "Clathrate hydrates," *Ind. Eng. Chem. Res.*, **32**, 1255 (1993).
- Handa, Y. P. and Stupin, D. Y., "Thermodynamic properties and dissociation characteristics of methane and propane hydrates in 70-Å-radius silica gel pores," *J. Phys. Chem.*, **96**, 8599 (1992).
- Jeffrey, G. A., *Inclusion compounds*, Vol. 1, Academic Press, London (1984).
- Kim, D.-Y., Uhm, T.-W. and Lee, H., "Compositional and structural identification of natural gas hydrates collected at site 1249 on ocean drilling program leg 204," *Korean J. Chem. Eng.*, **22**, 569 (2005).
- Kvenvolden, K. A., *International conference on natural gas hydrates*, Vol. 715, Ann. N. Y. Acad. Sci. (1994).
- Lee, H., Seo, Y., Seo, Y.-T., Moudrakovski, I. L. and Pipmeester, J. A.,

- "Recovering methane from solid methane hydrate with carbon dioxide;" *Angew. Chem. Int. Ed.*, **115**, 5202 (2003).
- Lee, J.-W., Chun, M.-K., Lee, K.-M., Kim, Y.-J. and Lee, H., "Phase equilibria and kinetic behavior of CO₂ hydrate in electrolyte and porous media solution: application to ocean sequestration of CO₂," *Korean J. Chem. Eng.*, **19**, 673 (2002a).
- Lee, K.-M. and Lee, H., "CO₂ hydrate behavior in the deep ocean sediments; phase equilibrium, formation kinetics, and solubility;" *Geophysical Research Letters*, **29**, 1029 (2002b).
- Makogon, Y. F., *Natural gas hydrate: the state of study in the USSR and perspectives for its use*, the 3rd International Chemical Congress of North America, Toronto, Canada (1988).
- Ridley, I. and Dominic, K., "Gas hydrates keep energy on ice;" *New Sci.*, **117**, 53 (1988).
- Seo, Y., Lee, H. and Uchida, T., "Methane and carbon dioxide hydrate phase behavior in small porous silica gels: three-phase equilibrium determination and thermodynamic modeling;" *Langmuir*, **18**, 9164 (2002).
- Sloan, Jr. E. D., *Clathrate hydrates of natural gases*, 2nd ed., Marcel Dekker, New York (1998).
- Sloan, Jr. E. D., "Fundamental principles and applications of natural gas hydrates;" *Nature*, **426**, 353 (2003).