METHANE EXPLOITATION BY CARBON DIOXIDE FROM GAS HYDRATES —PHASE EQUILIBRIA FOR CO$_2$-CH$_4$ MIXED HYDRATE SYSTEM—

KAZUNARI OHGAKI, KIYOTERU TAKANO,
HIROYUKI SANGAWA, TAKUYA MATSUBARA,
AND SHINYA NAKANO
Dept. of Chem. Eng., Osaka Univ., Toyonaka, 560

Key Words: Energy Resource, Natural Gas Exploitation, CO$_2$ Isolation, Environmental Problem, Gas Hydrate

Natural-gas hydrate fields having a large amount of methane deposits have become the object of public attention as a potential natural-gas resource. An idea of methane exploitation in linkage with CO$_2$ isolation has been presented elsewhere. In the present study, the isothermal phase equilibrium relations of pressure and compositions in the gas, liquid, and hydrate phases for the CO$_2$-CH$_4$ mixed hydrate system at 280 K are obtained in company with the apparent Henry constants for the methane-water system and the three-phase coexisting lines for the methane hydrate system. The averaged distribution coefficient of methane between gas phase and hydrate phase is about 2.5, that is, methane in the hydrate phase is replaced selectively by CO$_2$. This is the first experimental evidence for the possibility of methane exploitation combined with CO$_2$ isolation.

Introduction

Gas hydrates of crystalline substances are composed of an open water network of host water molecules arranged to prepare small and large cages capable of entrapping guest molecules. Gas hydrates have been a source of problems in the energy industry because it was recognized that the plugging of natural-gas pipelines was due to formation of gas hydrates of natural-gas (Hammerschmidt, 1934).

From a different point of view, gas hydrates have recently attracted the attention of many investigators of petroleum and chemical engineering, and earth and environmental science. For example: 1) the idea for CO$_2$ storage on the sea floor has been proposed as one of the projects of holding the CO$_2$ concentration below a given level (Ohgaki and Inoue, 1994); CO$_2$ hydrate is formed at a certain depth and aggregates forming a solid layer of hydrate which effectively prevents molecules of the stored gas from diffusing out into the sea; 2) natural-gas deposits in the form of solid gas hydrates occur in the subterranean regions of the Arctic and in the bottom of the sea at various places in the world (Kvenvolden, 1988, Englezos, 1993). These methane hydrates may produce a potentially enormous “green house” feed back effect on the future global climate. This positive feedback will result because of the large amount of “green house” methane that could be released from gas hydrate fields. On the other hand, the large amounts of methane hydrates are regarded as a future energy resource (Kvenvolden, 1988, Stevens, 1988), although no effective and concrete methods are available for natural-gas exploitation. We have pointed out that there is the possibility of exploitation of natural-gas from gas hydrate field in linkage with the environmental problem of CO$_2$ isolation, that is, the CO$_2$ supplied to the hydrate field could dissociate the methane hydrate and be semipermanently stored there as CO$_2$ hydrate (Ohgaki et al., 1994).

However, methane replacement by CO$_2$ in gas hydrates would require a quantitative understanding of the thermodynamics and kinetics of hydration. The phase equilibrium of the CO$_2$-CH$_4$ mixed hydrate is especially essential to natural-gas exploitation linked to CO$_2$ isolation.

In the present study, gas solubilities of methane in liquid water are measured at elevated pressures. The three-phase coexistence line (pressure and temperature relation) of gaseous methane-saturated water-methane hydrate is also measured in addition to the previous measurement of CO$_2$ solubilities in liquid water and the pressure-temperature relation of gaseous CO$_2$-liquid water-CO$_2$ hydrate (Ohgaki et al., 1993).

For the CO$_2$-CH$_4$ mixed hydrate system, an isothermal phase equilibrium relation of pressure-gas phase composition-hydrate composition is determined under conditions of three-phase coexistence. The proposed process combined with natural-gas exploitation and CO$_2$ isolation is briefly discussed from experimental results obtained in the present study.

* Received on November 28, 1995. Correspondence concerning this article should be addressed to Kazunari Ohgaki.
1. Experimental

1.1 Experimental apparatus

The experimental apparatus used in this study consists of four major sections; an equilibrium cell equipped with a magnetic agitator, a sample supplying system, a pressure-temperature measurement system, and a composition analyzing system.

Equilibrium cell: A schematic diagram of the equilibrium cell built for the present study is shown in Fig. 1. The equilibrium cell (ca. 150 cm³ in volume and allowing a maximum pressure of 15 MPa) was made of stainless steel and has a pair of windows on opposite sides which permits observation of the presence of gas hydrates and phase behavior. The contents of the cell are agitated by a mixing stick (made of SUS 630) externally driven with a permanent magnet which moves up and down. The up-and-down agitation is quite important for preventing the crystallization of gas hydrates at only the interface between the liquid and gas phases. The effective inner volume of the cell was calibrated by weighing on a precision balance (accuracy of ±0.1 mg and max. 3 kg, Cho balance).

Sample-supplying system: The gas-sample charging system consisted of a gas cylinder for weighing the total amount of substances supplied to the equilibrium cell. The total amount of water supplied to the cell was also measured by the same method as the above. Before the specified amount of water was charged, a known amount of gas sample was supplied at the desired pressure under vacuum.

Pressure-temperature measurement system: The equilibrium pressure was measured using a calibrated pressure transducer (Valcom VPRT) located close to the cell. The accuracy of the pressure measurement was estimated to be within 5 kPa. The temperature was controlled by a programming thermo-controller (Taitec PU-9) and was measured with an accuracy of ±0.01 K by using a thermometer (Takara D-641). Data of both quantities were stored in a recorder and a personal computer.

Composition analyzing system: For a mixed hydrate system, the composition of gas phase in equilibrium at a given temperature and pressure was measured directly by a gas chromatograph (Shimadzu GC-7AG). The gas-phase composition was analyzed for CO₂ and methane as the composition of water in the gas phase is negligibly small in the present experimental conditions. A small amount of gas phase was expanded into a container of variable volume and was introduced into a gas chromatograph. The composition was determined by direct comparison of the peak area ratio of the unknown sample with that of a known standard of similar concentration.

![](image)

Fig. 1 Schematic illustration of equilibrium cell

1.2 Measurement of gas-solubility and three-phase coexistence line

The inner volume of the equilibrium cell and the quantities of sample gas and water charged in the cell were known previously. Therefore, the temperature-pressure measurement allows calculation of gas-solubility in the water from the material balance, assuming that the mole fraction of water in the gas phase is zero.

After gas solubility measurements, an excess of gas was added to react through hydration under isothermal conditions. Although hydration was nearly finished in the first 2–3 hours, the three-phase coexisting mixture was left to stand undisturbed overnight. When maximum sorption was attained, the three-phase coexistence point was obtained by measuring the equilibrium temperature and pressure. As the above methods were described in a previous paper (Ohgaki et al., 1993), the details are not mentioned here.

1.3 Experimental procedure for mixed hydrate system

A specified amount of CO₂ was supplied to the volume-calibrated equilibrium cell under vacuum. A known amount of methane was then added to prepare a gas mixture of about 0.3 – 0.4 mol in the total amount of substances. After gas-mixing, a known amount of water (about 1 – 1.2 mol) was introduced to the cell by using a high-pressure pump. All amounts of substances supplied were quantified by weighing on a precision balance and allowed to react in an amount of more than 0.1 mol of mixed gas-hydrates under the three-phase coexisting conditions. By continued agitation, the contents of the cell were established in equilibrium. In Fig. 1, the cell containing CO₂, methane, water and the mixed hydrate in equilibrium are shown schematically. After the pressure-temperature measurement, a small amount
of gas phase was taken out and the composition analyzed by gas chromatography. The variables measured directly in this experiment are as follows: the total volume, \( V \); each total quantity of CO\(_2\), methane and water, \( n_1 \), \( n_2 \) and \( n_3 \), respectively; equilibrium temperature, \( T \); equilibrium pressure, \( p \); and mole fractions of gas phase, \( y_1 \) and \( y_2 \). The composition in the mixed hydrate system is calculated from the material balance in combination with the above data and the volumetric properties evaluated from the equation of state for gas-mixtures. Materials Research grade methane of purity 99.95 mol\% and CO\(_2\) of purity 99.99 mol\% were obtained from Takachiho Trading Co., Ltd. and used without further purification. Water was purified by distillation followed by deionization.

2. Results and Discussion

2.1 Gas-solubilities at elevated pressure

As the volume of the equilibrium cell and the total amount of each component supplied were known, we introduce the assumptions that the partial molar volume of methane dissolved in the liquid water was equal to that of infinite dilution at a given temperature, and that the gas phase in equilibrium was almost pure methane. Thus the apparent Henry constants are evaluated from the data of vapor-liquid equilibrium before hydration occurs, the apparent Henry constant, \( H_1(T, p) \), can be correlated as a function of temperature, \( T \), and pressure, \( p \), within 1\% error near the three-phase coexisting line.

\[
H_2(T, p)/\text{MPa} = (-1859 + 4.645 T/K)
\]

\[
\exp[\nu_1(p - 7.285 \text{ MPa})/RT]
\] (1)

The gas-solubilities of CO\(_2\) in water were presented elsewhere (Ohgaki et al., 1993),

\[
H_1(T, p)/\text{MPa} = (-468.4 + 1.985T/K)
\]

\[
\exp[\nu_2(p - 2.238 \text{ MPa})/RT]
\] (2)

where the subscripts 1 and 2 denote CO\(_2\) and methane respectively, \( R \) is the gas constant, and \( \nu_i \) is the partial molar volume at a given temperature. The mole fraction of each component in the liquid phase, \( x_i \), is obtainable at a given temperature and pressure.

\[
x_i = f_i(T, p)/H_i(T, p)
\] (3)

where \( f_i(T, p) \) is the fugacity calculated from the recommended equations of state (Angus et al., 1976a, 1976b).

2.2 Pressure-temperature relation for pure hydrate system

The pressure-temperature relations for the CO\(_2\)-water-hydrate and methane-water-hydrate systems are schematically shown in Fig. 2. As described previously (Ohgaki and Hamanaka, 1995), the CO\(_2\)-water-hydrate system has four three-phase coexisting curves originating from the quadruple point of 283.17 K and 4.50 MPa. On the other hand, the methane-water-hydrate system has one three-phase coexisting curve of linear increase in the present experimental conditions. The curve of interest is the three-phase coexisting of H-L1-G (refer to the caption of Fig. 2), which is correlated by the Clapeyron equation.

\[
\ln(p_1^{1}/\text{MPa}) = 4.8770 - 8894 K/T + 4.695 \ln(T/K)
\] (4)

\[
\ln(p_2^{1}/\text{MPa}) = -531.7 - 15854 K/T + 84.609 \ln(T/K)
\] (5)

where the superscript s denotes the saturated state under three-phase coexisting and the subscripts are the same to the above. Both the correlation equations give a good agreement with the data reviewed by Sloan (1990).

It is clear that there is an interesting zone where CO\(_2\) hydrate can grow up although methane hydrate is dissociated at a given temperature and pressure. The existence of the shaded zone in Fig. 2 is essential to study the operation conditions of replacement of natural-gas (methane) by CO\(_2\) in a gas-hydrate field.

2.3 Phase equilibrium for mixed hydrate system

The main purpose of the present study is to elucidate the phase equilibria for the CO\(_2\)-CH\(_4\) mixed hydrate system under three-phase coexisting conditions. The formula of mixed hydrate is generally written by \( z \text{CO}_2 \cdot (1-z)\text{CH}_4 \cdot q\text{H}_2\text{O} \), where \( z \) is the mole fraction of CO\(_2\) in the hydrate phase and \( q \) denotes the hydration number of the ideal gas-hydrate.
Table 1 Isothermal equilibrium data for CO$_2$(1)-CH$_4$(2)-H$_2$O system under three-phase coexistence at 280.3 K

<table>
<thead>
<tr>
<th>$p$ [MPa]</th>
<th>$z_1$</th>
<th>$y_1$</th>
<th>$x_1^i$ (H$_2$O free)</th>
<th>$p$ [MPa]</th>
<th>$z_1$</th>
<th>$y_1$</th>
<th>$x_1^i$ (H$_2$O free)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.04</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.22</td>
<td>0.44</td>
<td>0.241</td>
<td>0.63</td>
</tr>
<tr>
<td>3.24</td>
<td>0.84</td>
<td>0.683</td>
<td>0.92</td>
<td>4.31</td>
<td>0.39</td>
<td>0.215</td>
<td>0.59</td>
</tr>
<tr>
<td>3.38</td>
<td>0.80</td>
<td>0.585</td>
<td>0.88</td>
<td>4.32</td>
<td>0.36</td>
<td>0.217</td>
<td>0.59</td>
</tr>
<tr>
<td>3.60</td>
<td>0.67</td>
<td>0.488</td>
<td>0.83</td>
<td>4.34</td>
<td>0.37</td>
<td>0.203</td>
<td>0.57</td>
</tr>
<tr>
<td>3.64</td>
<td>0.69</td>
<td>0.450</td>
<td>0.80</td>
<td>4.37</td>
<td>0.35</td>
<td>0.203</td>
<td>0.57</td>
</tr>
<tr>
<td>3.67</td>
<td>0.68</td>
<td>0.448</td>
<td>0.82</td>
<td>4.37</td>
<td>0.36</td>
<td>0.183</td>
<td>0.54</td>
</tr>
<tr>
<td>3.71</td>
<td>0.61</td>
<td>0.429</td>
<td>0.79</td>
<td>4.44</td>
<td>0.36</td>
<td>0.179</td>
<td>0.53</td>
</tr>
<tr>
<td>3.77</td>
<td>0.60</td>
<td>0.384</td>
<td>0.76</td>
<td>4.50</td>
<td>0.35</td>
<td>0.169</td>
<td>0.52</td>
</tr>
<tr>
<td>3.86</td>
<td>0.59</td>
<td>0.357</td>
<td>0.75</td>
<td>4.57</td>
<td>0.32</td>
<td>0.144</td>
<td>0.47</td>
</tr>
<tr>
<td>3.98</td>
<td>0.53</td>
<td>0.302</td>
<td>0.70</td>
<td>4.58</td>
<td>0.32</td>
<td>0.141</td>
<td>0.46</td>
</tr>
<tr>
<td>4.00</td>
<td>0.52</td>
<td>0.310</td>
<td>0.70</td>
<td>4.63</td>
<td>0.29</td>
<td>0.143</td>
<td>0.47</td>
</tr>
<tr>
<td>4.01</td>
<td>0.55</td>
<td>0.311</td>
<td>0.71</td>
<td>4.75</td>
<td>0.24</td>
<td>0.104</td>
<td>0.38</td>
</tr>
<tr>
<td>4.06</td>
<td>0.51</td>
<td>0.288</td>
<td>0.68</td>
<td>4.85</td>
<td>0.23</td>
<td>0.090</td>
<td>0.34</td>
</tr>
<tr>
<td>4.07</td>
<td>0.52</td>
<td>0.293</td>
<td>0.69</td>
<td>4.99</td>
<td>0.16</td>
<td>0.065</td>
<td>0.27</td>
</tr>
<tr>
<td>4.15</td>
<td>0.47</td>
<td>0.268</td>
<td>0.66</td>
<td>5.46</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4.20</td>
<td>0.45</td>
<td>0.245</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The volume-balance in the equilibrium cell is given as

$$V = \Sigma n_i^G v_m^G + \Sigma n_i^L v_m^L + n_i^H v_m^H$$ (6)

where the subscript m stands for the gas-mixtures and the superscripts H, L, and G denote the hydrate phase, liquid phase, and gas phase, respectively.

The following three equations should be satisfied because of the material balance for each component.

$$n_i^i = n_i^G + n_i^L + z n_i^H$$ (7)

$$n_i^i = n_i^G + n_i^2 + (1-z) n_i^H$$ (8)

$$n_i^i = n_i^1 + q n_i^H$$ (9)

The expressions of mole fractions are as follows,

$$y_i = n_i^G / \Sigma n_i^G$$ (10)

$$x_i = n_i^1 / \Sigma n_i^1$$ (11)

$$x_2 = n_2^1 / \Sigma n_2^1$$ (12)

As explained in the experimental section, the values of $V$, $n_i$, $n_i^2$, $n_i^1$, $T$, $p$, $y_i$ are measured directly in the present study. We assumed that the values of $x_1$ and $x_2$ can be estimated from the apparent Henry constants of each pure-gas system. The molar volume of ideal hydrate of 130.1 cm$^3$/mol is calculated from the lattice constant of hydrate crystal. Also the volumetric properties were calculated from the Soave-Redlich-Kwong equation of state for gas-mixtures (Sloan, 1990) or the IUPAC recommended equation of state for pure substances (Angus et al., 1976a, 1976b). Finally, the seven unknown variables of $n_i^G$, $n_i^2$, $n_i^1$, $n_i^1$, $n_i^n$, and $z$ are obtained from the above seven simultaneous equations. Table 1 summarizes the isothermal phase equilibrium data ($p-x-y-z$ relation) for the CO$_2$-CH$_4$ mixed hydrate system at 280 K where the water-free mole fraction in the liquid phase, $x_1^i$, is defined as $x_1^i = x_1/(x_1+x_2)$. The maximum error in the evaluation of $z$ is estimated to be about 5%. The error is mainly induced from the assumption for gas-solubility especially when the value of $n_i^i$ is considerably large.

The fundamental thermodynamic properties of mixed hydrates can be estimated by van der Waals and Platteeuw’s method (1959) based on the Langmuir adsorption model. According to their model, the chemical potential is written as,

$$\Delta \mu = \mu_{\text{emp}}(T, p) - \mu_{\text{hyd}}(T, p, z)$$ (13)

where $\Delta \mu$ is the chemical potential difference between the occupied hydrate and the hypothetical empty hydrate lattice. For a mixed hydrate system, $\Delta \mu$ is given by using the cage occupation probability of gas molecules.

$$\Delta \mu = RT \Sigma n_i \ln(1 - \Sigma \theta_i)$$ (14)

where $\nu_i$ is the crystallographic constant of the hydrate cages. It is reasonable to assume that the CO$_2$-CH$_4$ mixed hydrate would form the crystal lattice of “structure I” because both the pure hydrates form the same lattice. The lattice of “structure I” consists of two different cages, “s”-cage and “m”-cage. The analogous description of occupation probability is applied to the Langmuir adsorption,
\[ \theta_{ij} = c_{ij} f_i (1 + \Sigma c_{ij} f_i) \]  

(15)

where \( c_{ij} \) is the Langmuir constant of \( i \)-component in the \( j \)-cage, and \( f_i \) is the fugacity of \( i \)-component. The value of \( c_{ij} \) is given by the integration of the total smoothed-cell Lennard-Jones potential (Parrish and Prausnitz, 1972). Therefore, the above model combined with the experimental data of \( T, p \) and \( y \) allows calculation of the occupation probability of each component in the two hydrate cages. The mole fraction of \( CO_2 \) in the mixed hydrate phase can be estimated from Eq. (16).

\[ z = \frac{\Sigma \nu_j \theta_{ij}^{(s)} \nu_j^{(s)} (\theta_{ij} + \theta_{ij}^{(m)})}{\Sigma \nu_j \theta_{ij}^{(m)}} \]  

(16)

where the subscript \( j \) stands for "s" and "m" cages.

Figure 3 shows phase equilibria for the \( CO_2-CH_4 \) mixed hydrate system at 280 K. The solid lines are smoothed values of experimental data for each phase and the broken line denotes the mole fraction in the hydrate phase estimated by van der Waals and Platteeuw’s model. The estimation of \( z \) does not show a good agreement with the experimental results, however, the outline of the \( p-z \) curve is satisfactory. Adisasmito et al. (1991) reported the \( p-y \) (gaseous phase only) relation for the same system and their data agree well with those of the present study as shown in Fig. 3.

The most important information is that the mole fraction of \( CO_2 \) in the mixed hydrate phase is considerably larger than that of the gas phase under the conditions of three-phase coexistence (the averaged distribution coefficient of methane, \( y_2 z_1 / y_1 z_2 \), is 2.5). In other words, methane in the hydrate cage is selectively replaced by \( CO_2 \) and the mole fraction of methane in the gas mixture becomes larger than that of mixed hydrate phase.

2.4 General statement of natural-gas exploitation from gas-hydrate fields

A brief discussion about the natural-gas exploitation combined with \( CO_2 \) storage under the outer continental margins at 1000 – 2000 m in subsurface depth is presented here on the basis of the present experimental results.

The process proposed is schematically shown in Fig. 4. \( CO_2 \) introduced to an exploitation cave, where the temperature and pressure are regulated to maintain the three-phase coexisting condition which corresponds to the shaded zone in Fig. 2. Under the isothermal condition (280 K was chosen as the operation temperature in the present study with regard to the geothermal gradient of ca. 1.6 K/100 m (Sloan, 1990)), the three-phase coexistence is expected in a pressure range of \( 3 - 5.5 \) MPa.

If the exploitation pressure is controlled at \( 4 \) MPa, the mole fraction of methane would be 0.7 in the gas-mixture which is exploited as natural-gas. The mole fraction of methane in the hydrate phase is 0.48 in equilibrium. The driving force of methane replacement by \( CO_2 \) is the mole-fraction difference between 0.48 (equilibrium) and the averaged value in the hydrate phase.

The \( CO_2 \) in this process fills one more important role of heat supply. It is pointed out that the methane hydrate has self-protection ability for pressure unstableness because of the large enthalpy change of hydrate dissociation (Handa, 1986). The heat of \( CO_2 \) hydration (exothermic reaction) exceeds the heat of methane hydrate dissociation (endothermic reaction), that is, the methane exploitation becomes possible by use of the heat of \( CO_2 \) hydration.
Conclusion

Isothermal phase equilibrium data of pressure-compositions in the gas, liquid, and hydrate phases are obtained for the CO₂–CH₄ mixed hydrate system at 280 K under the three-phase coexistence conditions.

The averaged distribution coefficient of methane between the gas phase and the hydrate phase is about 2.5, that is, methane in the hydrate phase is selectively replaced by CO₂ and the mole fraction of methane in the gas phase is larger than that of the mixed hydrate phase.

This fact is the first experimental evidence for supporting the possibility of methane exploitation from natural-gas fields by use of CO₂ stored there as gas hydrates.

Acknowledgment

This research was supported by a Grand-in-Aid for the Scientific Research Fund (No. 07650895) from the Ministry of Education, Science and Culture, Japan.

This research was also supported in part by the Kansai Electric Power Co., Inc. (The Kansai). To promote the research Institute for Laser Technology is left in charge of committee by The Kansai. The authors thank all of the committee members. The authors are also grateful to Dept. of Chem. Eng., Osaka Univ. for the scientific support by “Gas-Hydrate Analyzing System (GHAS)” constructed by a supplementary budget of 1995 from the Ministry of Education, Science, Sports and Culture, Japan.

Nomenclatures

\begin{align*}
\text{c} & = \text{Langmuir constant} \\
\text{f} & = \text{fugacity} \\
\text{H} & = \text{apparent Henry constant} \\
\text{n} & = \text{total amount of substance} \\
\text{p} & = \text{pressure} \\
\text{q} & = \text{hydration number} \\
\text{R} & = \text{gas constant} \\
\text{T} & = \text{temperature} \\
\text{V} & = \text{volume of equilibrium cell} \\
\text{v} & = \text{molar volume} \\
\text{x} & = \text{mole fraction of liquid phase} \\
\text{y} & = \text{mole fraction of gas phase} \\
\text{z} & = \text{mole fraction of hydrate phase} \\
\theta & = \text{cage occupation probability} \\
\mu & = \text{chemical potential of hydrate} \\
\nu & = \text{number of cages per H}_2\text{O molecule}
\end{align*}

Literature Cited


