Physical Data of CO$_2$ Hydrate

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1. Introduction

Gas hydrates are crystalline molecular complexes formed from mixtures of water and low molecular weight gases. The water molecules form a lattice without taking a lattice position; hydrates thus belong to the class of compounds known as clathrates. While the gas molecule (guest molecules in the hydrate phase are historically called gas molecules even when they are not in the gas phase) is enclosed within the lattice formed by the water molecules, there is no chemical union between the gas and water. Instead, the water molecules that form the lattice are strongly hydrogen bonded with each other and the gas molecules interact with the water molecules through van der Waals type dispersion forces. Study of crystal structures have shown that hydrates of non polar gases crystalline in either of two structures referred to as structure I and structure II, which are composed of polyhedral cages as drawn in Fig. 1. The water network structure is metastable and cannot be formed without at least partial occupation of the cavities by gas molecules. The formation of either structure I or structure II is dependent on the relative stabilities of the two structures. Figure 2 illustrates the structures of various hydrate forming gases [11].

In this review, the physical properties of CO$_2$ hydrate are introduced with a number of numerical data. Prior to the listing of each data, some review papers for several categories of the gas hydrate study are introduced.

2. Review Articles about Gas Hydrates

Stackelberg and co-workers studied the gas hydrates from 1940 to 1950 and were the first to characterize their two basic crystal structures by means of X-ray powder diffraction patterns [32]. The crystal structure aspects were reviewed by Jeffrey and McMullan [15]. Davidson [7] reviewed their structures with emphasis on the dynamical information obtained from dielectric and NMR spectroscopy method.

The fundamental model is based on classical statistical thermodynamics and
is used to predict the thermodynamic behavior of gas hydrates including the pressures and temperatures at which hydrates form. An early, basic form of the model was first presented by van der Waals and Platteeuw [36] and is based upon classical adsorption theory. Using this model, some investigators developed, generalized and simplified the methods to predict hydrate equilibria conditions. The recent improved form of the thermodynamic model was reviewed by Holder et al. [11]. Belosludov et al. [3] reviewed the theory of non-ideal clathrates with taking into account the interaction of the guests with each other.

Considerable work has done studying the physical properties of gas hydrates, such as hydrate composition, crystal densities, lower and upper invariant points, $P$-$T$ phase equilibrium data and their relationship, and so on. Chen [5] carried out the detailed study about the determination of the composition and phase diagram of CO$_2$ hydrate. Suwandi [34] reviewed many of the important physical properties of 51 gas hydrates and agents that form them.
Fig. 2. Molecules which form the clathrate hydrates, arranged in order to molecular size. [7] with partially modifications.

3. Physical Properties of CO₂ Hydrate

3.1 Physical properties of CO₂

Table 1 lists some important properties of carbon dioxide. The sources of data were International Critical Tables [14] (no superscription), Suwandi [34]*, Himmelblau [9]**, Chen [5]# and Miller and Smythe [23]##.
Table 1. Physical properties of carbon dioxide (as for references, see text).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight:</td>
<td>44.000 g/mole</td>
</tr>
<tr>
<td>Boiling point:</td>
<td>-78.5 °C</td>
</tr>
<tr>
<td>Melting point:</td>
<td>-56.2 °C</td>
</tr>
<tr>
<td>Critical point:</td>
<td>31.1 °C at 73.0 atm</td>
</tr>
<tr>
<td>Vapor pressure of the liquid:</td>
<td>56.495 atm at 20°C</td>
</tr>
<tr>
<td></td>
<td>34.379 atm at 0°C</td>
</tr>
<tr>
<td></td>
<td>19.437 atm at -20°C</td>
</tr>
<tr>
<td>Density of the gas:</td>
<td>1.9769 kg/m³ at 0°C, 1 atm</td>
</tr>
<tr>
<td>Density of the solid:</td>
<td>1.565 kg/m³ at -80°C, 1 atm</td>
</tr>
<tr>
<td>Density of the liquid*:</td>
<td>857 kg/m³ at the critical point</td>
</tr>
<tr>
<td>Solubility in water:</td>
<td>1.55 cm³ CO₂/cm³ H₂O at 25°C, 1 atm</td>
</tr>
<tr>
<td></td>
<td>16.3 cm³/cm³ at 20°C, 25 atm</td>
</tr>
<tr>
<td></td>
<td>20.1 cm³/cm³ at 20°C, 35 atm</td>
</tr>
<tr>
<td></td>
<td>23.9 cm³/cm³ at 20°C, 45 atm</td>
</tr>
<tr>
<td></td>
<td>*31.0 cm³/cm³ at the critical point</td>
</tr>
</tbody>
</table>

Diffusion coefficient of dissolved CO₂ gas in water**:  
- 0.960 x 10⁵ cm²/sec at 0°C
- 1.17 - 1.28 x 10⁵ cm²/sec at 10°C
- 1.60 - 1.77 x 10⁵ cm²/sec at 20°C
- 1.75 - 2.29 x 10⁵ cm²/sec at 30°C

Latent heat of fusion:  
189.6 J/g at -56.2°C

Latent heat of vaporization:  
577 J/g at -78.5°C (solid)
288 J/g at -20°C
234 J/g at 0°C

Heat of solution of CO₂ in water*: -19.90 kJ/g mole

Apparent activation energy for adsorption*: 24.7 kJ/mole

3.2 Structure of CO₂ hydrate

Stackelberg and Müller [31] and Claussen [6] studied the structure of water molecules in CO₂ hydrate crystals by using X-rays. They suggested that the structure of the hydrate is a unit cell consisting of 46 water molecules enclosing
Table 2. Geometry of unit cells and cages [7].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group, cell parameter</td>
<td>Pm3n, 12.03Å (12.04Å [34])</td>
</tr>
<tr>
<td>Number of water molecule</td>
<td>46</td>
</tr>
<tr>
<td>Nonequivalent O site</td>
<td>6(c), 16(i), 24(k)</td>
</tr>
<tr>
<td>Oxygen site symmetry</td>
<td>42m, 3m, m</td>
</tr>
<tr>
<td>Departure of O--O--O angle from tetrahedral</td>
<td></td>
</tr>
<tr>
<td>Average at O site</td>
<td>1.2°, 1.2°, 5.1°</td>
</tr>
<tr>
<td>Average in structure</td>
<td>3.7°</td>
</tr>
<tr>
<td>Average O--O length</td>
<td>2.793Å</td>
</tr>
<tr>
<td>Small cages</td>
<td></td>
</tr>
<tr>
<td>Number, symmetry</td>
<td>2, m3</td>
</tr>
<tr>
<td>Oxygen sites</td>
<td>8(i), 12(k)</td>
</tr>
<tr>
<td>Distance to center</td>
<td>3.83Å, 3.96Å</td>
</tr>
<tr>
<td>Average cage radius</td>
<td>3.91Å</td>
</tr>
<tr>
<td>Average free diameter</td>
<td>about 5.0Å§</td>
</tr>
<tr>
<td>Large cages</td>
<td></td>
</tr>
<tr>
<td>Number, symmetry</td>
<td>6, 42m</td>
</tr>
<tr>
<td>Oxygen sites</td>
<td>4(c), 8(i), 8(k), 4(k)</td>
</tr>
<tr>
<td>Distance to center</td>
<td>4.25, 4.47, 4.06, 4.645Å</td>
</tr>
<tr>
<td>Average cage radius</td>
<td>4.33Å</td>
</tr>
<tr>
<td>Average free diameter</td>
<td>about 5.8Å§</td>
</tr>
</tbody>
</table>

(Van der Waals radius of water molecule: 1.4Å)

two small holes and six larger ones into which CO₂ molecules can pack. This structure is referred to structure I (see Fig. 1).

Some geometric parameters for structure I were listed by Davidson [7], which are given Table 2.

3.3 P-T phase diagram for the CO₂-H₂O-Hydrate system

Larson [20] worked out the phase diagram of the carbon dioxide-water system. He sketched three equilibrium curves with temperature ranging from −16°C to 12°C. These curves were (a) the equilibrium between gaseous carbon
dioxide CO$_2$ (g), liquid carbon dioxide CO$_2$ (l) and hydrate; (b) the equilibrium between CO$_2$ (g), hydrate and aqueous solution; (c) the equilibrium between CO$_2$ (g), hydrate and ice. Takenouchi and Kennedy [35] studied the phase diagram of CO$_2$ hydrate in the condensed region at high pressure and at temperature above
Table 3. Critical decomposition condition, invariant point with ice, and empirical equations [5].

\[
\Delta \mu_w^* = 1120 \text{ J/mol} \\
\Delta h_w^* = 1714 \text{ J/mol} \\
\text{(in the liquid water region subtract 601J/mol from } \Delta h_w^*) \\
\Delta v_w = 2.9959 \text{ cm}^3/\text{mol} \\
\text{(in the liquid water region add 1.6 J/mol to } \Delta v_w) \\
\Delta C_{pw} = -34.583 + 0.189(T - T_0) \text{ J/mol } (T > T_0), \ T_0 = 273.15 K \\
\Delta C_{pw} = 3.315 + 0.21(T - T_0) \text{ J/mol } (T < T_0)
\]

Fig. 4. Complete known phase diagram of CO$_2$-H$_2$O-Hydrate (CO$_2$·7.30H$_2$O) [5].

10°C up to 19.5°C. The equilibrium curve they determined was for the equilibrium between CO$_2$ (l), solution and hydrate.

Chen [5] compiled the data of the phase equilibria obtained by Larson [20] and those obtained by their own measurements. These data were then fitted to equations by the least square method, and listed in Table 3. A phase diagram for the CO$_2$-H$_2$O-Hydrate system has been constructed in Fig. 3.
A complete known phase diagram has been summarized by Chen [5] and plotted in Fig. 4. The following is a list of the data sources:

Line AB, A'B', A"B", AD: Chen [5]
Line BC: Larson [20]
Line AE: Takenouchi and Kennedy [35]
Line KD, DJ: Vukalovich and Altumn [38]
Line GH: Miller and Smythe [23]

In the diagram point D, 216.55°C and 5.112 atm, is the triple point of pure carbon dioxide. Line KD is the equilibrium line of solid CO₂ and liquid CO₂. Line AE, the equilibrium CO₂(l) + nH₂O(l) ←→ CO₂nH₂O(s), has about the same shape as line KD; that is, the effect of pressure on the melting point of solid CO₂ is very similar to its effect on the melting point of the hydrate. Line BF will reach 0°C as the pressure goes to zero. This line represents the depression of the freezing point of water due to dissolved CO₂. Miller and Smythe predict that lines GH and DJ will intersect at 121.22°K and 2.481 × 10⁻⁴ atm (0.2 mmHg). The phase diagram for the CO₂-NaCl-H₂O-Hydrate system (lines A'B' and A"B" in Fig. 4) studied by Chen [5] will be shown in the later section.

3.4 Composition and density of CO₂ hydrate

The compositions of the hydrate determined by various workers and the methods they used are summarized by Chen [5]. Then he accurately measured the decomposition pressures of CO₂ hydrate in NaCl aqueous solution of different concentration. The composition of the hydrate was determined from 31 experimental points by using Miller-Strong’s method [22] to be:

\[ n = 7.30 \pm 0.13 \text{ moles of water per mole of hydrate.} \]

No trend that \( n \) is a function of temperature was observed over the range -1.5° to 10°C.

The density of the hydrate can be calculated with both geometrical and thermodynamic methods. The density as calculated from X-ray investigation is 1.134 g/cm³ [35], and that based on \( n = 7.3 \) is 1.054 g/cm³ [5]. On the other hand, the density calculated by using the Clausius-Clapeyron equation and the heat of formation of the hydrate, obtained by Larson, was reported to be 1.15 g/cm³ [35]. With the correction of Larson’s data, the result comes out to be 1.112 g/cm³ [5].

Chen [5] and Bozzo et al. [4] have recommended the value for the density of CO₂ hydrate to be 1.112 g/cm³. The difference of the values calculated from two methods is only 2%.

3.5 Heats of formation of CO₂ hydrate

The heats of the reactions were measured by Villard [37] and calculated by Larson [20]. Larson has reported the standard heat of formation of CO₂, \( \Delta H^\circ \), by using van der Waal’s equation to calculate the volume of gaseous carbon dioxide.
Table 4. Heats of formation of CO$_2$ hydrate calculated from phase equilibrium data with $n = 7.30$ [5].

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CO$_2$: a thin rod core, H$_2$O: a point molecule</td>
<td>$l: 2.30$ Å, $\sigma: 3.36$ Å, $\varepsilon/k: 309$ K</td>
</tr>
<tr>
<td>(2) CO$_2$: a spherical core, H$_2$O: a spherical core</td>
<td>$2a: 0.720$ Å, $\sigma: 2.9681$ Å, $\varepsilon/k: 169.09$ K</td>
</tr>
<tr>
<td>(3) CO$_2$: a modified spherical core, H$_2$O: a spherical core</td>
<td>$a_g: 0.677$ Å, $a_w: 0$ Å, $\sigma_g: 3.407$ Å, $\sigma_w: 3.56438$ Å, $\varepsilon_g/k: 506.25$ K, $\varepsilon_w/k: 102.134$ K, $\varepsilon/k: 227.39$ K</td>
</tr>
</tbody>
</table>

The parameters for the empirical function:
- small cage: $a_0 = 35.3446$, $n = 0.973$
- large cage: $a_0 = 14.1161$, $n = 0.826$
- $\omega = 0.225$

$l$: the core length for a rodlike molecule
$a$: the core radius of interaction for gas & water molecules
$\sigma$: the core to core distance between a gas & a water molecule
$\varepsilon$: the depth of the intermolecular well
$k$: Boltzmann’s constant

Van der Waal’s equation is not very accurate at temperatures near the critical point, and at 8.5°C, gives a molar volume of carbon dioxide which is 10% higher than the experimental value.

Chen [5] calculated the heat of formation of CO$_2$ hydrate from phase equilibrium data by using Piereon and Korvezze’s method and the hydrate composition obtained from the Miller-Strong method, i.e. $n = 7.30$. He corrected Larson’s results and showed the good agreement of the corrections with his results. Table 4 is the results of the heats of reaction of the four equilibria calculated by Chen [5].
3.6 Thermodynamic properties and site occupancy of CO$_2$ hydrate

Van der Waals and Platteeuw [36] have derived the thermodynamic properties of gas hydrates from a single model. They considered the gas molecule moving about in a spherical cage formed by the water molecules and applied the Lennerd-Jones-Devonshire cell theory.

The method for predicting equilibrium is based on the criterion that at equilibrium $\mu_H = \mu_W$ where $\mu_H$ is the chemical potential of water in the hydrate phase, and $\mu_W$ is that in water rich or ice phase. Using $\mu_b$, the chemical potential of an unoccupied (hypothetical) hydrate lattice, as the reference state, the condition for equilibrium can be rewritten as

$$\Delta \mu_W = \Delta \mu_H$$  \hspace{1cm} (1)

where

$$\Delta \mu_W = \mu_b - \mu_W$$  \hspace{1cm} (2)

and

$$\Delta \mu_H = \mu_b - \mu_H.$$  \hspace{1cm} (3)

The reference properties of the structure I hydrate to calculate $\Delta \mu_W$ [18] are listed in Table 5.

For calculation of (CO$_2$) hydrate equilibria, the following equation is solved

$$\Delta \mu_H = RT \sum v_i \ln \left( 1 + C_i \phi y_p \right)$$  \hspace{1cm} (4)

where $v_i$ is the ratio of cavities (of type $i$) to water molecules in the hydrate phase ($v_1 = 1/23$, $v_2 = 3/23$), $\phi$ and $y$ are the fugacity coefficient and mole fraction, respectively, of gas species (CO$_2$) which is in equilibrium with the hydrates. The dependence of $\Delta \mu_H$ on temperature and pressure are described by Holder et al. [10].

Equation (4) can be numerically solved for pressure if the Langmuir constant $C$ is known. The smooth-cell Langmuir constant is (without subscripting):

$$C = \frac{4 \pi^R}{\kappa T_o} \left[ \exp \left( -w(r) / kT \right) \right] r^2 dr$$  \hspace{1cm} (5)

where $w(r)$ is the smoothed cell radial potential function obtained using the appropriate potential; it is specific to each cavity-gas combination. Here $r$ is the radial distance of the enclathrated gas molecule from the cavity center.

Van der Waals and Platteeuw [36] originally used the Lennard-Jones 12-6
Table 5. Reference properties of Structure I hydrate [18].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical decomposition point A</td>
<td>10.00 °C, 44.40 atm</td>
</tr>
<tr>
<td>Invariant point with ice B</td>
<td>-1.48 °C, 10.28 atm</td>
</tr>
</tbody>
</table>

Constants in Equation (T: absolute temperature, P: atm)):

\[
\text{CO}_2(g) + n\text{H}_2\text{O}(\text{ice}) \leftrightarrow \text{Hydrate (Line BC)}
\]
\[
\ln P = 13.50880616 - 3036.897979 / T
\]

\[
\text{CO}_2(g) + \text{Hydrate} \leftrightarrow \text{CO}_2(l) + \text{Hydrate (Line AD)}
\]
\[
\ln P = 10.75411787 - 1971.035206 / T
\]

\[
\text{CO}_2(g) + n\text{H}_2\text{O}(l) \leftrightarrow \text{Hydrate (Line AB)}
\]
\[
\ln P = -58105.56177 + 8185.485312 \ln T + 4430531.757 / T - 300893013 / T^2
\]

for the temperature range -1.5° to +9°C

\[
\ln P = 50.112966 - 13114.749 / T
\]

for the range +9° to +10°C

potential to represent the interaction between enclathrated gas and hydrate lattice water molecules.

McKoy and Sinanoglu [24] suggested use of the Kihara potential function after comparing predicted and experimental results and concluding that the Lennard-Jones function was satisfactory only for small spherical molecules while the Kihara function gave better results for larger polyatomic and rodlike molecules. The Kihara potential assigns a core to each molecules. It therefore includes the effect of the finite size of the molecules on their interaction. The core of CO₂ molecules is defined as the line segment between the nuclei of oxygen, e.g., the O-O distance while that of water molecules, as the point.

Parrish and Prausnitz [28] generalized the model of gas hydrate by use of the Kihara spherical-core potential.

Recently John and Holder [16], [17] and John et al. [18] have eliminated many of the restraints by making appropriate modification to the model. They calculated the excellent cell potential at a given radical and angular location of the gas molecule by summing the binary interactions of the gas molecule with each of the water molecules, whose coordinates were determined through X-ray crystallography. In order to correct for the fact that actual guest-host interactions depart from the spherical smooth cell potential, they introduced an empirical function that corrected the Langmuir constant due to the restricted motion of
Table 6. Kihara parameters for carbon dioxide and water molecules used for three calculations.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH° (kJ/g-mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂(g) + nH₂O(l) ⇔ CO₂ nH₂O(s)</td>
<td>-ΔH° = 59.91</td>
</tr>
<tr>
<td>reaction with water</td>
<td></td>
</tr>
<tr>
<td>CO₂(g) + nH₂O(s) ⇔ CO₂ nH₂O(s)</td>
<td>-ΔH° = 23.93</td>
</tr>
<tr>
<td>reaction with ice</td>
<td></td>
</tr>
<tr>
<td>CO₂(g) + CO₂ nH₂O(s) ⇔ CO₂(l) + CO₂ nH₂O(s)</td>
<td>-ΔH° = 11.72</td>
</tr>
<tr>
<td>(which is equal to the heat of condensation of CO₂)</td>
<td></td>
</tr>
<tr>
<td>CO₂(l) + nH₂O(l) ⇔ CO₂ nH₂O(s)</td>
<td>-ΔH° = 46.40</td>
</tr>
<tr>
<td>(the heat of fusion of the hydrate)</td>
<td></td>
</tr>
<tr>
<td>or -ΔH° = 48.20</td>
<td>(with the correction of the heat capacity change at constant pressure [4])</td>
</tr>
</tbody>
</table>

spherical gas molecules.

The Kihara parameters for CO₂-H₂O molecule with a smooth cell approximation used for these calculations mentioned above are listed in Table 6.

The site occupancy of small and large cages for CO₂ hydrate were calculated by McKoy and Sinanogle [24] using the Kihara potential. They obtained:

θ₁ = 0.528, θ₂ = 0.879

where θ₁ and θ₂ are the site occupancies of small and large cages for structure I, respectively.

Using these data, the density of CO₂ hydrate calculated through geometrical method results in about 1.054 g/cm³. This is good agreement with the experimental data obtained by Chen [5] (see Subsection 3.4). More detailed and direct measurements for the density and site occupancy for CO₂ hydrate are required.

3.7 Phase behavior in the presence of NaCl

The determination of the effect of hydrate inhibitors, especially salts, is important for a hydrate process for separating saline solutions into water and solid salt. The process had been described in 1960's [1], [18]. Chen [5] studied the pressure-temperature-concentration data for CO₂ hydrate in NaCl solutions for engineering use.

Pressure-temperature measurement in 5 and 10% salt solutions are shown in
Fig. 5. Experimental phase diagram for CO$_2$-NaCl-H$_2$O-Hydrate system in saturated salt region [5].

Fig. 5 (dotted lines are obtained by a least square fit to the experimental data) [5]. By assuming the hydrating number $n = 7.30$ and using Miller-Strong's method in reverse, a set of pressure ($P$)-temperature ($T$)-concentration ($W$) data is obtained. Table 7 represents the calculated values of $P-T-W$ [4].
Table 7. Calculated P-T-W data for CO₂-H₂O-NaCl system with n = 7.30 [4], pressure in atm for NaCl solution (wt%).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>0%</th>
<th>2.5%</th>
<th>5%</th>
<th>7.5%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.48</td>
<td>10.28</td>
<td>11.49</td>
<td>12.96</td>
<td>14.81</td>
<td>17.23</td>
</tr>
<tr>
<td>0</td>
<td>12.15</td>
<td>13.61</td>
<td>15.40</td>
<td>17.66</td>
<td>20.67</td>
</tr>
<tr>
<td>2</td>
<td>15.29</td>
<td>17.19</td>
<td>19.53</td>
<td>22.56</td>
<td>26.70</td>
</tr>
<tr>
<td>4</td>
<td>19.41</td>
<td>21.93</td>
<td>25.09</td>
<td>29.30</td>
<td>35.34</td>
</tr>
<tr>
<td>6</td>
<td>25.00</td>
<td>28.48</td>
<td>32.97</td>
<td>39.31</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>32.86</td>
<td>37.98</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>44.40</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Critical temp. °C</td>
<td>10.00°</td>
<td>8.80°</td>
<td>7.54°</td>
<td>6.16°</td>
<td>4.60°</td>
</tr>
</tbody>
</table>

The data can be converted for use with sea water by dividing the weight percent NaCl by 0.927 to give wt% sea salts.

The effect of the NaCl concentration on the critical decomposition temperature for the range 0 to 16 wt% NaCl can be expressed by the following equation:

\[
W = 0.05286(10.0 - t)(t + 29.361)
\]  

(6)

with \( W = \text{wt}% \text{ NaCl in solution, and } t = \text{°C} \), by using a least square fit to a second degree equation. This reproduces the concentration with an average deviation of 2.1% and a maximum of 5.7%, e.g. at \( t = 0 \text{°C} \), \( W = 15.52 \pm 0.33\% \text{ NaCl} \).

Direct measurement of the depression of the critical decomposition temperature by NaCl up to salt saturation gave the eutectic point at which five phases are present with three components. The phases are solid hydrate, solid NaCl₂H₂O, liquid CO₂, aqueous saturated solution, and gas. The invariant eutectic point thus found and the temperature-pressure data are shown in Fig. 5. Chen [5] and Bozzo et al. [4] took the H₂O-CO₂-NaCl eutectic conditions to be:

\( t = -9.6\text{°C} \),
\( P = 26.47 \text{ atm} \),
\( W = 24.2 \text{ wt% NaCl} \).

4. Other Topics on Gas Hydrates

In this chapter, some important articles of the gas hydrate studies classified into the different categories from those in the previous chapter are reviewed.

4.1 Kinetics of formation and dissociation of gas hydrates

As we showed in the previous chapter, the thermodynamics of gas hydrates
have been studied extensively for more than three decades the kinetics of formation and decomposition, however, have only recently been investigated.

Vysniauskas and Bishnoi [39], [40] reviewed the published information on the kinetics of formation of gas hydrates, but in such studies, no quantitative model was developed to predict the mass of gas hydrates formed with respect to time. Simulation or modelling of the reaction processes between gas (or liquid) and water (or sea water) requires an understanding and description of the kinetics of gas hydrate formation and dissociation.

Bishnoi and co-workers has carried out the theoretical and experimental work in 1980’s and their understanding of the thermodynamics and the kinetics of formation and decomposition of gas hydrates is presented by Englezos et al. [8]. Although their experiments were performed not on the carbon dioxide-water system, but on the systems of methane, ethane, or their mixture, and water, their model of gas hydrate is considered to be adoptable for the CO₂ hydrate system.

Past CO₂ concentration changes in the atmosphere can be determined with high confidence by analyzing the air enclosed in the pores of the ice obtained from both Greenland [33] and Antarctic [2] ice sheet. The CO₂ changes revealed from Vostok ice core, Antarctica, for instance, are well correlated with the antarctic temperature record derived from the ice isotopic profile measured on the same core. Such a high correlation would be expected if CO₂ plays an important role in forcing the climate.

Lorius et al. [21] have reviewed the data from cores drilled in polar ice sheets. They predicted that the future warming induced by the greenhouse gases such as carbon dioxide and methane depends critically on the sensitivity of the climate of the Earth to increasing atmospheric concentrations of these gases. Many palaeoclimate data are used to assess the role of greenhouse gases in explaining past global climate change, and the validity of models predicting the effect of increasing concentrations of such gases in the atmosphere.

4.2 Formation of CO₂ hydrate in the deep sea

Sediments containing carbon dioxide and methane hydrates are naturally found in regions of permafrost and beneath the sea in outer continental margins. Because methane hydrates occurs in the shallow geosphere, they are of interest as a potential resource of natural gas and as a possible cause of global warming due to the methane released to the atmosphere. The presence of CO₂ hydrates has also been predicted in organic-rich marine sediments but not previously observed.

Recently, the natural CO₂ hydrate formation were observed on the sea floor at 1335–1550 m depth in the hydrothermal field, mid-Okinawa Trough [29], [30]. CO₂-rich fluid bubbles, including approximately 86% CO₂, were venting at the sea floor. Gas hydrates were then immediately formed on the surface of the bubbles and these hydrates coalesced to form pipes standing on the sediments. In order to understand the behavior, the experimental studies have been carried out both in the ocean [12] and in the laboratory [26].
The storage of CO₂ recovered from thermal power plants in the ocean are considered to be one of the effective measures to control the increase in atmospheric CO₂. Some studies of the feasibility and technology of CO₂ storage in the ocean have been started [25], [27].

REFERENCES


