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# Ice–Clathrate Hydrate–Gas Phase Equilibria for Air, Oxygen, Nitrogen, Carbon Monoxide, Methane, or Ethane + Water System<sup>†</sup>

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In this work, we report ice–clathrate hydrate–gas equilibrium data (dissociation data) for the air, oxygen, nitrogen, carbon monoxide, methane, or ethane + water system. The equilibrium data for methane and ethane clathrate hydrates are compared with the equilibrium data reported in the literature to demonstrate the reliability of the isothermal pressure-search method used in our measurements. The equilibrium data generated for nitrogen and oxygen clathrate hydrates are compared with few sets of experimental data reported in the literature. It is shown that the existing ice–clathrate hydrate–gas equilibrium data reported in the literature for the nitrogen or oxygen + water system are not reliable. A comparison is finally made on the equilibrium conditions of air, oxygen, nitrogen, and carbon monoxide clathrate hydrates.

## 1. Introduction

Clathrate hydrates or gas hydrates are icelike crystalline compounds, which are formed through a combination of water and suitably sized guest molecule(s), like methane and ethane.<sup>1</sup> In clathrate hydrates, a guest molecule(s) is (are) trapped inside cages of hydrogen bonded water molecules.<sup>1</sup> A comprehensive study of clathrate hydrates is given elsewhere.<sup>1</sup> It has been proven that air, oxygen, nitrogen, and carbon monoxide can form clathrate hydrates.<sup>1–10</sup> However, phase equilibrium information for the clathrate hydrates of these molecules is limited.

Kuhs et al.<sup>3</sup> reported three ice–hydrate–gas (IHG) equilibrium data (dissociation data) for air clathrate hydrates in graphical form. Five liquid water–hydrate–gas (L<sub>w</sub>HG) equilibrium data for air clathrate hydrates were reported by Mohammadi et al.<sup>2</sup> in tabulated form. Van Cleeff and Diepen<sup>4,5</sup> and Mohammadi et al.<sup>2</sup> reported the L<sub>w</sub>HG equilibrium data for oxygen clathrate hydrates in tabulated form. Kuhs et al.<sup>3</sup> presented two IHG equilibrium data for oxygen clathrate hydrates in graphical form. Van Cleeff and Diepen<sup>4</sup> presented twelve IHG equilibrium data for oxygen clathrate hydrates in tabulated form. The L<sub>w</sub>HG equilibrium data for nitrogen clathrate hydrates were reported by van Cleeff and Diepen,<sup>4,5</sup> Marshal et al.,<sup>6</sup> Jhaveri and Robinson,<sup>7</sup> and Mohammadi et al.<sup>2</sup> in tabulated form. Miller<sup>8,9</sup> and Kuhs et al.<sup>3</sup> reported one and four IHG equilibrium data, respectively, for nitrogen clathrate hydrates in graphical form. Van Cleeff and Diepen<sup>4</sup> presented twelve IHG equilibrium data for nitrogen clathrate hydrates in tabulated form. Mohammadi et al.<sup>10</sup> reported the L<sub>w</sub>HG equilibrium data for carbon monoxide clathrate hydrates in tabulated form. To our knowledge, there is no IHG equilibrium data for carbon monoxide clathrate hydrates. This literature review shows a need for generating more and reliable equilibrium data for clathrate hydrates of air, oxygen, nitrogen, and carbon monoxide, especially for the IHG equilibrium conditions.

The main objective of this work is to report the IHG equilibrium data for the air, oxygen, nitrogen, or carbon monoxide + water system. An isothermal pressure-search method<sup>11–13</sup> was used to generate these data. The reliability of

this technique<sup>11–13</sup> was first examined by generating some experimental data for the IHG equilibrium of the methane or ethane + water system, for which sufficient experimental data have been reported in the literature.<sup>1</sup> The good agreement between our experimental data and those reported in the literature for clathrate hydrates of methane and ethane demonstrates the reliability of the experimental method used in this work.

## 2. Experimental Section

**2.1. Materials.** Table 1 reports the purities and suppliers of the materials used in this work.

**2.2. Experimental Apparatus.** Briefly, the main part of the apparatus is a sapphire cylindrical vessel, which can withstand pressures up to 15 MPa. The volume of the vessel is 33.1 cm<sup>3</sup>. A stirrer was installed in the vessel to agitate the gas, liquid water/ice, and hydrate crystals inside it. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperatures and check for their equality within temperature measurement uncertainties, which are estimated to be less than 0.1 K. This temperature uncertainty estimation comes from calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel was measured with a DRUCK pressure transducer (Druck, type PTX611 for pressure ranges up to 14 MPa). Pressure measurement uncertainty is estimated to be less than 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

**2.3. Experimental Method.** To measure the equilibrium conditions, a trial and error procedure was used.<sup>11–13</sup> The system temperature was kept constant at desired value in each experiment. After the system had stabilized, the pressure drop was monitored as hydrates formed.<sup>11,13</sup> The pressure drop occurred due to encapsulation of the gas molecules in the hydrate

**Table 1. Purities and Suppliers of Materials<sup>a</sup>**

gas	supplier	purity, mol %
air	Air Liquide	>99.9
oxygen	Air Liquide	>99.9
nitrogen	Air Liquide	>99.9
carbon monoxide	Air Liquide	>99.9
methane	Messer Griesheim	99.995
ethane	Messer Griesheim	99.995

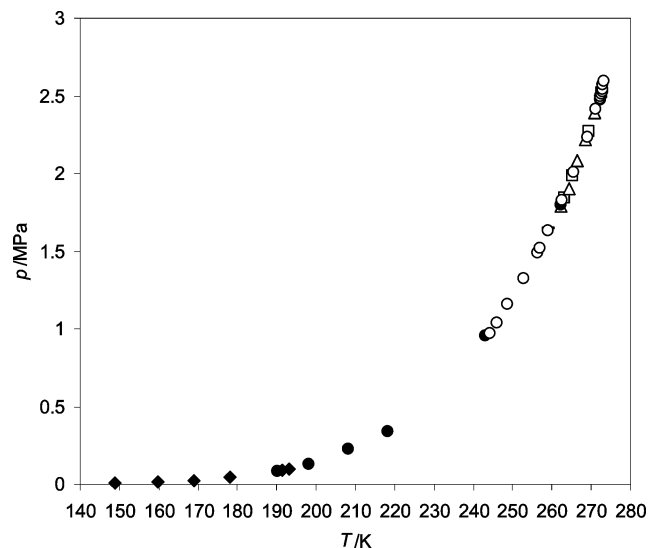
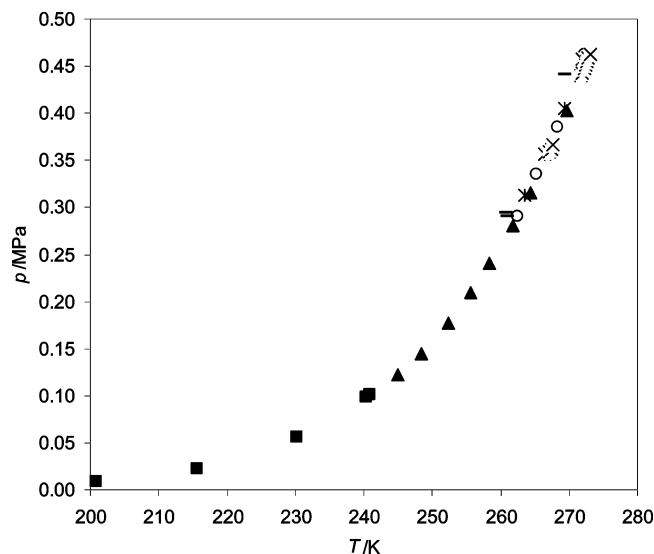
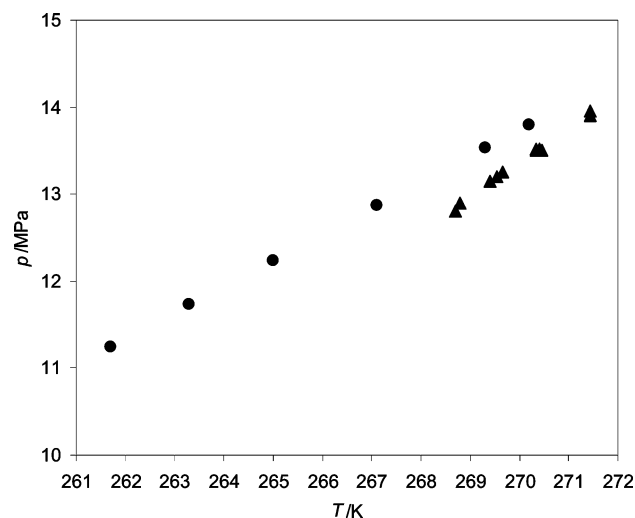
<sup>a</sup> Deionized water was used in all experiments.

<sup>†</sup> This manuscript was presented at the AIChE Annual Meeting 2009 in Nashville, TN.

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**Table 2. IHG Equilibrium Data (Dissociation Data) for the Air, Oxygen, Nitrogen, Carbon Monoxide, Methane, or Ethane + Water System**

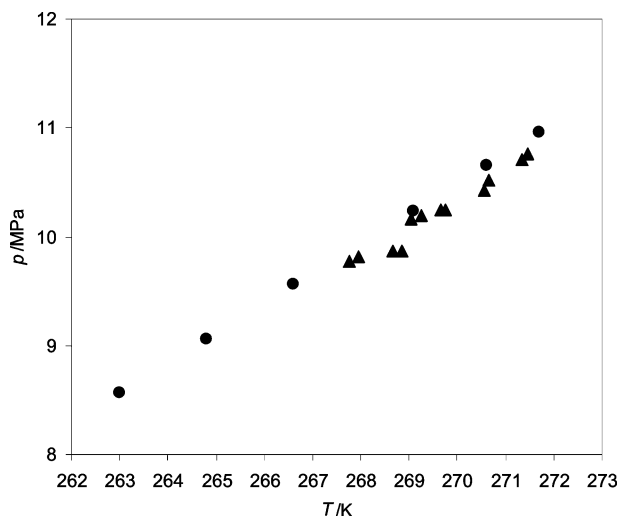
$T/K$	$p/\text{MPa}$
air clathrate hydrates	
271.3	12.94
269.8	12.52
268.1	12.04
266.6	11.62
265.3	11.25
263.5	10.74
oxygen clathrate hydrates	
271.7	10.96
270.6	10.66
269.1	10.24
266.6	9.56
264.8	9.06
263.0	8.57
nitrogen clathrate hydrates	
270.2	13.80
269.3	13.53
267.1	12.87
265.0	12.24
263.3	11.73
261.7	11.25
carbon monoxide clathrate hydrates	
271.8	13.61
270.2	13.08
268.6	12.48
265.7	11.66
264.2	11.18
262.3	10.54
methane clathrate hydrates	
272.6	2.52
269.4	2.27
265.2	1.98
263.2	1.84
ethane clathrate hydrates	
272.2	0.462
268.3	0.385
265.2	0.336
262.5	0.290

**Figure 1.** Experimental equilibrium (dissociation) conditions of methane clathrate hydrates (ice–hydrate–gas equilibrium). Symbols represent experimental data: (–) ref 14; ( $\Delta$ ) ref 15; ( $\blacklozenge$ ) ref 16; ( $\bullet$ ) ref 11; ( $\circ$ ) ref 17; ( $\square$ ) this work.**Figure 2.** Experimental equilibrium conditions of ethane clathrate hydrates (ice–hydrate–vapor equilibrium). Symbols represent experimental data: (–) ref 14; ( $*$ ) ref 15; ( $\blacksquare$ ) ref 18; ( $\blacktriangle$  and  $\times$ ) ref 17; ( $\circ$ ) this work.**Figure 3.** Experimental equilibrium conditions of nitrogen clathrate hydrates (ice–hydrate–gas equilibrium). Symbols represent experimental data: ( $\blacktriangle$ ) ref 4; ( $\bullet$ ) this work.

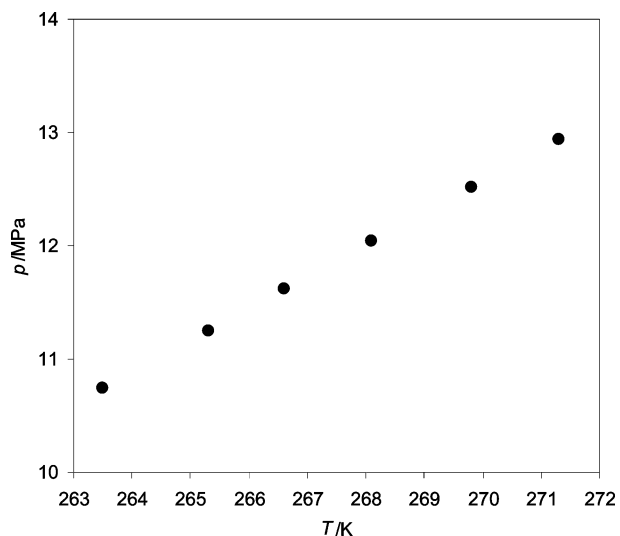
phase.<sup>12,13</sup> When the pressure approached a near-equilibrium value, some gas was vented from the system.<sup>11,13</sup> Upon system shut-in, if the pressure increased, hydrate decomposed, and the system was below the hydrate equilibrium pressure.<sup>12,13</sup> However, if the pressure continued to decrease after partial venting of the gas, the system was above the hydrate equilibrium pressure.<sup>12,13</sup> Assuming that the pressure increased, in subsequent cycles, the cell was recharged slightly above the original stabilized value. Again a drop in the pressure indicated that the system was above the hydrate equilibrium pressure, and that hydrate formation had resumed.<sup>12,13</sup> This process was repeated in successive approximations until the differential between the lower formation and upper decomposition pressures was low.<sup>12,13</sup> The average of the upper and lower pressure approximations was taken as the equilibrium value at the given temperature.<sup>11,13</sup>

### 3. Results and Conclusion

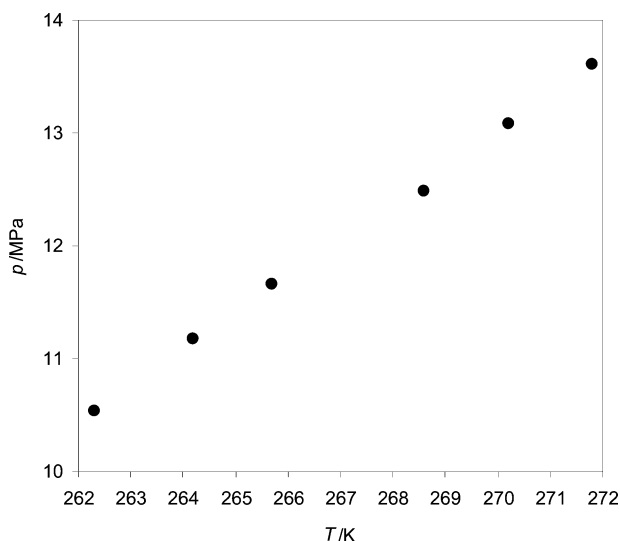
All the equilibrium data measured in this work are reported in Table 2, and are shown in Figures 1–7. Figures 1–4 also show the experimental data reported in the literature. In Figures



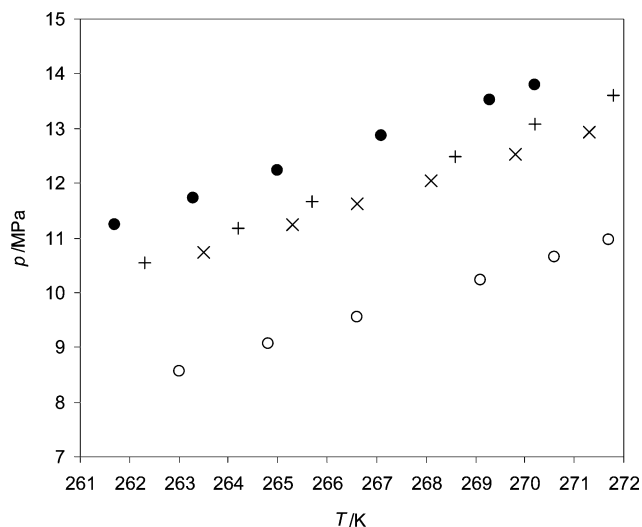
**Figure 4.** Experimental equilibrium conditions of oxygen clathrate hydrates (ice-hydrate-gas equilibrium). Symbols represent experimental data: (▲) ref 4; (●) this work.



**Figure 5.** Experimental equilibrium conditions of air clathrate hydrates (ice-hydrate-gas equilibrium). Symbols represent experimental data: (●) this work.



**Figure 6.** Experimental equilibrium conditions of carbon monoxide clathrate hydrates (ice-hydrate-gas equilibrium). Symbols represent experimental data: (●) this work.



**Figure 7.** Comparisons of experimental equilibrium conditions for air, nitrogen, oxygen, and carbon monoxide clathrate hydrates (ice-hydrate-gas equilibrium). Symbols represent experimental data measured in this work: (●) nitrogen clathrate hydrates; (○) oxygen clathrate hydrates; (×) air clathrate hydrates; (+) carbon monoxide clathrate hydrates.

3–5, the graphical data of Kuhs et al.<sup>3</sup> for nitrogen, oxygen, and air clathrate hydrates, respectively, have not been shown due to difficulties in reading these data. In Figures 1 and 2, the good agreement between the experimental data reported in our work for methane and ethane clathrate hydrates (which form hydrates at relatively intermediate and low pressures, respectively) with the experimental data reported in the literature demonstrates the reliability of the experimental method<sup>11–13</sup> used in our work. In Figures 3 and 4, the IHG equilibrium data reported by van Cleeff and Diepen<sup>4,5</sup> for the nitrogen or oxygen + water system, respectively, show large deviations from our experimental data indicating the latter data are not reliable. The comparison between the IHG equilibrium data for the air, oxygen, nitrogen, or carbon monoxide + water system in Figure 7 shows that the dissociation temperatures at given pressures can be summarized as: nitrogen clathrate hydrates > carbon monoxide clathrate hydrates > air clathrate hydrates > oxygen clathrate hydrates.

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