

# Equilibrium Data of Nitrous Oxide and Carbon Dioxide Clathrate Hydrates<sup>†</sup>

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In this communication, we report equilibrium pressures for nitrous oxide clathrate hydrates in the temperature range of (266.7 to 285.1) K and for clathrate hydrates of carbon dioxide in the temperature range of (264.5 to 271) K. The experimental data have been measured using isochoric pressure search methods. It is shown that the dissociation temperatures of nitrous oxide clathrate hydrates are approximately 2.3 K higher than the dissociation temperatures of carbon dioxide clathrate hydrates at given pressures.

## Introduction

Gas hydrates, or clathrate hydrates, are solid crystalline compounds stabilized by the inclusion of suitably sized guest molecules inside cavities, of different sizes, formed by water molecules through hydrogen bonding.<sup>1</sup> They resemble ice in appearance, but unlike ice, they may form at temperatures well above the ice point.<sup>1</sup> The most common gas hydrate structures are those of structure I (sI) and structure II (sII), where each structure is composed of a certain number of large and small cavities formed by water molecules.<sup>1</sup> Nitrous oxide is a suitably sized molecule, which can form the structure I gas hydrate.<sup>1</sup> Currently, very limited information is available in the literature for this clathrate hydrate.<sup>1,2</sup> In 1888, Villard<sup>2</sup> reported that nitrous oxide forms gas hydrates. This gas is similar in molecular weight to carbon dioxide. It may therefore be assumed that carbon dioxide and nitrous oxide simple hydrates can have similar hydrate characteristics, as a similar argument was made for carbon monoxide and nitrogen simple hydrates, which have the same molecular weights.<sup>3</sup> However, it has recently been demonstrated that carbon monoxide hydrates form at temperatures lower than the corresponding temperatures for nitrogen hydrates.<sup>4</sup> It is therefore the intention of this work to study phase boundaries of carbon dioxide and nitrous oxide simple hydrates. The experimental apparatus is based on our previous experimental work,<sup>5,6</sup> which takes advantage of isochoric pressure search methods.<sup>4–12</sup> The dissociation pressures have been measured for nitrous oxide hydrates in the temperature range of (266.7 to 285.1) K and for hydrates of carbon dioxide in the temperature range of (264.5 to 271) K. The dissociation data of nitrous oxide hydrates are compared with the dissociation data of carbon dioxide and nitrous oxide simple hydrates reported in the literature<sup>2,4,10,12</sup> and the experimental data generated in this work on hydrate dissociation data of carbon dioxide. It is demonstrated that nitrous oxide hydrates are dissociated at temperatures higher than the corresponding temperatures for carbon dioxide hydrates.

## Experimental Section

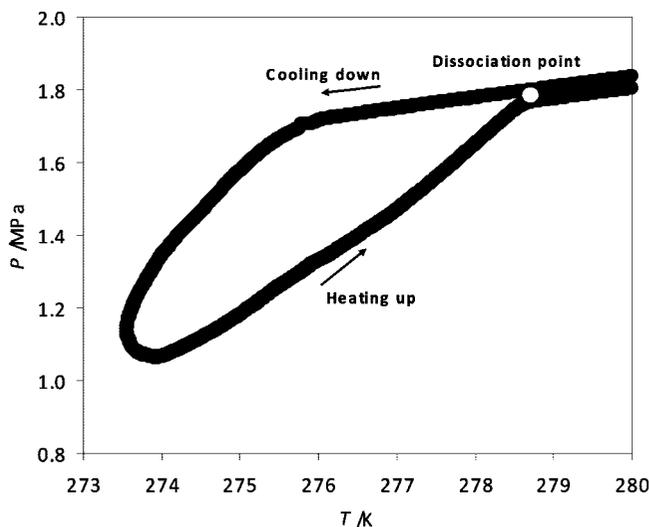
Nitrous oxide and carbon dioxide were purchased from Air Liquide with certified purities higher than 99.998 %. Deionized water was used in all experiments.

A detailed description of the experimental setup used in this study is given elsewhere.<sup>5,6</sup> Briefly, the main part of the apparatus is a cylindrical vessel with two sapphire windows, which can withstand pressures higher than 40 MPa. The volume of the vessel is 57.5 cm<sup>3</sup>. A stirrer was installed in the vessel to agitate the fluid and hydrate crystals inside it. The vessel was immersed inside a temperature-controlled bath to maintain the temperature inside it at a prescribed level. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperature and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from careful calibration against a 25  $\Omega$  reference platinum resistance thermometer. The pressure in the vessel was measured with two DRUCK pressure transducers (Druck, type PTX611 for pressure ranges up to (4 and 20) MPa, respectively). Pressure measurement uncertainties are estimated to be less than 5 kPa, as a result of careful calibration against a dead weight balance (Desgranges and Huot, model 520).

The liquid water + hydrate + vapor equilibrium conditions were measured with an isochoric pressure search method.<sup>4–7</sup> The vessel containing pure water (50 % by volume of the vessel was filled by water) was immersed into the temperature-controlled bath, and the gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the partially evacuated vessel. After obtaining temperature and pressure stability (far enough from the hydrate formation region), the valve in the line connecting the vessel and the cylinder was closed. Subsequently, temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was detected by a pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, temperature was kept constant with sufficient time to achieve a steady equilibrium state in the vessel. In this way, a pressure–temperature diagram was obtained for each experimental run, from which we determined the hydrate dissociation point (Figure 1).<sup>4–7,11</sup> If the temperature is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in the phase equilibria of the fluids in the vessel.<sup>4–7,11</sup> Consequently, the point at which the slope of pressure–temperature data plots changes sharply is considered to be the point at which all hydrate crystals have dissociated and hence is reported as the dissociation point.<sup>4–7,11</sup>

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**Figure 1.** Pressure–temperature diagram for estimating the hydrate dissociation point of nitrous oxide (278.7 K and 1.76 MPa).

To measure ice + hydrate + vapor equilibrium conditions, a trial and error procedure was used.<sup>8</sup> The system temperature was kept constant at a desired value in each experiment. After the system had stabilized, the pressure drop was monitored as hydrates formed.<sup>8</sup> The pressure drop occurred due to encapsulation of the gas molecules in the hydrate phase.<sup>9</sup> When the pressure approached a near-equilibrium value, some gas was vented from the system.<sup>8</sup> Upon system shut-in, if the pressure increased, the hydrates decomposed, and the system was below the hydrate equilibrium pressure.<sup>9</sup> However, if the pressure continued to decrease after partial venting of the gas, the system was above the hydrate equilibrium pressure.<sup>9</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>9</sup> This process was repeated in successive approximations until the differential between the lower formation and upper decomposition pressures was low.<sup>9</sup> The average of the upper and lower pressure approximations was taken as the equilibrium value at the given temperature.<sup>8</sup>

## Results and Discussion

All experimental dissociation data measured in this work are reported in Tables 1 and 2 and are plotted in Figure 2. This figure also shows the experimental data reported in the literature for carbon dioxide<sup>4,10,12</sup> and nitrous oxide<sup>2</sup> simple hydrates. As can be observed, the two experimental data reported by Villard<sup>2</sup> for the liquid water + hydrate + vapor equilibria of nitrous oxide hydrates show a slight deviation from our experimental data; however, the agreements are generally acceptable. The experimental data for the liquid water + hydrate + vapor equilibria of carbon dioxide hydrates reported by Fan and Guo<sup>12</sup> and Mohammadi et al.<sup>4</sup> also show acceptable agreements, though the experimental data of Fan and Guo<sup>12</sup> show some deviations at high temperatures. Limited data are available for the ice + hydrate + vapor equilibria of carbon dioxide hydrates.<sup>1</sup> It was therefore decided to generate few equilibrium data for carbon dioxide hydrates in this region and study the reliability of the literature data.<sup>10</sup> As can be seen, the agreements between the experimental data generated in this work for the ice + hydrate + vapor equilibria of carbon dioxide hydrates with the experimental data of Larson<sup>10</sup> are generally acceptable, dem-

**Table 1.** Experimental Dissociation Data for Nitrous Oxide Clathrate Hydrates

$T/K^a$	$P/MPa^b$
Liquid Water + Hydrate + Vapor Equilibria	
285.1	4.13
284.5	3.78
283.6	3.30
282.8	2.94
281.7	2.54
281.0	2.33
279.6	1.97
278.7	1.76
277.0	1.44
275.4	1.21
273.3	0.99
Ice + Hydrate + Vapor Equilibria	
271.2	0.91
269.8	0.85
268.1	0.79
266.7	0.74

<sup>a</sup> Uncertainty on temperatures through calibrated platinum resistance thermometers is estimated to be less than 0.1 K. <sup>b</sup> Uncertainty on pressures through the calibrated pressure transducers is estimated to be less than 5 kPa.

**Table 2.** Experimental Dissociation Data for Carbon Dioxide Clathrate Hydrates

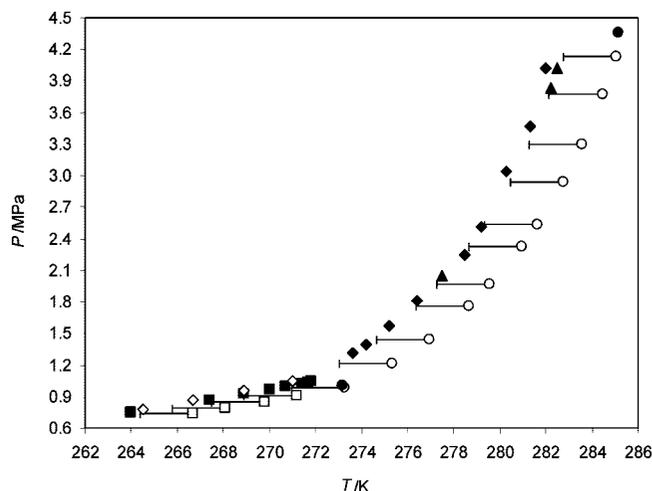
$T/K^a$	$P/MPa^b$
Ice + Hydrate + Vapor Equilibria	
271.0	1.05
268.9	0.96
266.7	0.87
264.5	0.78

<sup>a</sup> Uncertainty on temperatures through calibrated platinum resistance thermometers is estimated to be less than 0.1 K. <sup>b</sup> Uncertainty on pressures through the calibrated pressure transducers is estimated to be less than 5 kPa.

onstrating the reliability of the experimental technique<sup>8,9</sup> used in this work for measuring ice + hydrate + vapor equilibria. This technique<sup>8,9</sup> was then used to estimate the ice + hydrate + vapor equilibria of nitrous oxide hydrates. As can be observed in Figure 2, the ice + hydrate + vapor equilibria of nitrous oxide hydrates form at pressures lower than the corresponding pressures for carbon dioxide hydrates at given temperatures. In Figure 2, we have shown the temperature difference bands, which show that the dissociation temperatures of nitrous oxide hydrates are approximately 2.3 K higher than the hydrate dissociation temperatures of carbon dioxide at given pressures. This proves that although nitrous oxide and carbon dioxide have the same molecular weights their clathrate hydrate characteristics are different. This conclusion is similar to what was concluded for simple hydrates of nitrogen and carbon monoxide, which have the same molecular weights but different hydrate characteristics.<sup>4</sup>

## Conclusions

We reported experimental hydrate dissociation data for nitrous oxide in the temperature range of (266.7 to 285.1) K and for carbon dioxide in the temperature range of (264.5 to 271) K. The experimental data were measured using isochoric pressure search methods.<sup>4–12</sup> The two hydrate dissociation data reported by Villard<sup>2</sup> in 1888 for nitrous oxide are generally in acceptable agreement with the experimental data reported in our work. The comparison between the experimental hydrate dissociation data for nitrous oxide and carbon dioxide showed that the dissociation temperatures of nitrous oxide clathrate hydrates are approxi-



**Figure 2.** Experimental phase boundaries of nitrous oxide and carbon dioxide clathrate simple hydrates in the presence of pure water. Symbols, experimental data: ○, nitrous oxide hydrates in equilibrium with vapor and liquid water, this work; □, nitrous oxide hydrates in equilibrium with vapor and ice, this work; ●, nitrous oxide hydrates in equilibrium with vapor and liquid water, literature data;<sup>2</sup> ◇, carbon dioxide hydrates in equilibrium with vapor and ice, this work; ■, carbon dioxide hydrates in equilibrium with vapor and ice, literature data;<sup>10</sup> ▲, carbon dioxide hydrates in equilibrium with vapor and liquid water, literature data;<sup>4</sup> ◆, carbon dioxide hydrates in equilibrium with vapor and liquid water, literature data.<sup>12</sup> Bands: 2.3 K.

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