

## Methane Hydrate–Ice Equilibria in Porous Media

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Reported in this work are equilibrium pressures for the dissociation of methane hydrate confined in silica gel pores of nominal radii 7.5, 5.0, 3.0, or 2.0 nm. Also reported are equilibrium pressures for a sample containing a mixture of silica gel with nominal radii of 7.5 and 3.0 nm. Each of these porous media contained a broad distribution of pore radii. At higher temperatures, where the equilibria involved hydrate and liquid water, the pressures were larger than those for bulk hydrate at the corresponding temperature, and in general increased with a decrease in nominal pore radius. At lower temperatures where the equilibria involved ice, the pressures were identical (within expected experimental uncertainties) for all of the silica gels, and were the same as those reported in the literature for bulk methane hydrate. The independence of the equilibrium pressure from pore size at lower temperatures (where the equilibrium involved ice) indicates that for temperatures below the quadruple point temperature of the smallest hydrate containing pore, there is no detectable effect on the equilibrium pressure due to the restricted geometries of the porous media. This result suggests (1) that the interface relevant to the decomposition of hydrate in silica gel pores is that between the hydrate and the aqueous phase, as suggested by Henry et al.,<sup>1</sup> and either (2a) that within experimental error the surface energy between the hydrate and the aqueous phase can be approximated by that between ice and the appropriate aqueous phase or (2b) that  $\cos\theta$  for the contact angle of the hydrate–ice interface silica gel is approximately zero.

### Introduction

Clathrate hydrates are solid solutions in which water molecules form cages via hydrogen bonds, and individual gas molecules are enclosed in many of these cages. Natural gas hydrates are mostly formed by smaller hydrocarbon molecules, in particular methane, and have long been studied because they can form in pipelines and block the flow of natural gas and petroleum. Natural gas hydrates also form in the earth's crust in arctic regions and beneath the seafloor around the margins of most continental shelves.

Naturally occurring hydrates are often found in the pore space of terrestrial or sub-seafloor sediments (Sloan<sup>17</sup>). Experimental<sup>2–8</sup> and modeling studies<sup>1,5,7,9–13</sup> of the effects of pore size on the thermodynamics of hydrate formation and dissociation have been reported in the literature. Many authors<sup>1,5,10,14</sup> have concurred that the thermodynamics of hydrates in porous media should be described by the van der Waals–Plaatuew equation<sup>15</sup> for bulk hydrates with the addition of a capillary pressure term of the form  $2V_L \cos(\theta) \sigma/r$ , where  $V_L$  is the molar volume of the aqueous phase,  $\theta$  is the contact angle,  $\sigma$  is the surface tension, and  $r$  is the radius of the pore. Except for the recent

work by our group,<sup>6</sup> most of the experimental and theoretical studies have focused on the decomposition of hydrates in porous media to liquid water. In initial interpretational studies,<sup>1,9</sup> two different ideas for the identity of the capillary interface, and thus for the value of the interfacial tension in the capillary pressure term, were suggested. However, neither value for the tension gave satisfactory agreement<sup>1,9</sup> of the modified van der Waals–Plaatuew equation with the experimental data.<sup>2</sup> Recent work<sup>5,8,11</sup> has demonstrated one method that can be used to account for the broad range of pore radii presenting some porous media.<sup>2,16</sup>

To adequately interpret experimentally observed hydrate equilibrium pressures in porous media, our group has previously presented<sup>5</sup> a conceptual model that allows for the determination of the pore size corresponding to each observed temperature ( $T$ ), pressure ( $P$ ) pair. The effective pore sizes obtained from a series of ( $T,P$ ) points can then be used to reconstruct pore volume distributions which can be compared with those obtained from nitrogen adsorption studies. The close correspondence of the distributions obtained from these two very different methods when the equilibrium involves liquid water<sup>5,8</sup> suggests that the correct value of the surface tension between the hydrate and liquid water is very close to that between ice and liquid water.

Henry et al.<sup>1</sup> assumed that the relevant interface was between the hydrate and aqueous phases, and used a value of 0.0267 J/m<sup>2</sup> for equilibria involving liquid water. [We note that Klauda and Sandler<sup>10</sup> presented a method for calculation of hydrate equilibrium pressures in porous media based on a different

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TABLE 1: Specifications of Samples and Cells

	cell number					
	1	2	3	4	5 <sup>a</sup>	5 <sup>a</sup>
nominal pore size <sup>b</sup> (nm)	2	3	5	7.5	7.5	3
density <sup>a</sup> (g/cm <sup>3</sup> )	0.6196	0.4898	0.4327	0.4057	0.4057	0.4898
cell vol (cm <sup>3</sup> )	55.6	55.6	55.6	55.6	55.6	
line vol (cm <sup>3</sup> )	1.2	1.3	1.3	1.4	2.1	
total vol (cm <sup>3</sup> )	56.8	56.9	57.0	57.0	57.8	
silica gel (g)	13.44	8.95	7.50	6.70	3.47	4.30
water (g)	7.47	7.47	7.52	7.49	3.87	3.59
sample vol <sup>c</sup> (cm <sup>3</sup> )	23.9	20.2	21.6	21.5	10.5	10.5
glass beads (cm <sup>3</sup> )	32.0	19.3	32.9	25.3	24.6	
headspace (cm <sup>3</sup> )	0.9	17.3	2.4	10.2	22.7	

<sup>a</sup> 50% water in nominal 3.0-nm pores and 50% water in nominal 7.5-nm pores. <sup>b</sup> Of silica gel. <sup>c</sup> Of silica gel plus water.

method, but used the same hydrate–water interface and interfacial tension as Henry et al.<sup>1]</sup> The calculations of Henry et al.<sup>1</sup> were only for temperatures above 273 K, and so did not directly address the decomposition of hydrate to free gas and ice. Clarke et al.<sup>9</sup> suggested that the equilibrium pressure should be greater in pores than in the bulk, even when the equilibrium involves ice. On the basis of the assumption that  $\sigma \cos(\theta)$  is very small for equilibria involving ice, we proposed<sup>5–7,12,13</sup> that at any temperature below its quadruple point, the equilibrium pressure for any size pore should be the same as that for the bulk at that temperature. In media containing a distribution of pore sizes, as long as the experimental temperature is below the quadruple point temperature of all of the smallest hydrate-containing pores, the equilibrium pressure for the sample would be the same as that for the bulk. In our previous work, the equilibrium pressures of ethane hydrate in porous silica gel of nominal radii 7.5, 5.0, or 3.0 nm were measured, and it was found that at low temperatures the equilibrium pressure was independent of pore size.<sup>6,7,13</sup> The current work presents experimental results for methane hydrate equilibria in silica gel of five different pore-size distributions; these also support the hypothesis that below the lowest quadruple point for the pores filled with hydrate in the silica gel samples, the equilibrium pressure–temperature line should be the same for all size pores.

### Experimental Methods and Materials

The experimental facility is similar to that described in our previous work,<sup>6</sup> except that the system has been modified to allow for the simultaneous measurement of the equilibrium pressure for five different samples of silica gel. The modification also includes the use of a computerized pressure reading system. Each cell had its own pressure transducer with a pressure range of 6.9 MPa and an accuracy of 0.2% of full scale. All of the pressure transducers were from Setra. During the hydrate formation stage, all of the cells were connected to the same gas inlet. After the formation of hydrate in all of the cells, the connecting valves were closed to isolate each cell from the rest. All of the cells were immersed in the same coolant media with temperatures controlled to  $\pm 0.1$  K throughout the experiment.

Methane with a purity of no less than 99.97% was obtained from Matheson. Five types of porous media were used. Four of the samples contained silica gels as supplied by Aldrich, and had nominal pore radii of 2, 3, 5, and 7.5 nm, and were in cells 1–4, respectively (Table 1). The sample in cell 5 was a mixture of nominal 3 and 7.5 nm silica gels. The composition of the silica gel in cell 5 was constructed such that the amount of water sorbed in the two silica gels was approximately the same (Table 1). The preparation of water-saturated silica gel and the hydrate formation were the same as described previously (Zhang et al.<sup>7</sup>). The total uptake of water by the silica gel in each set of

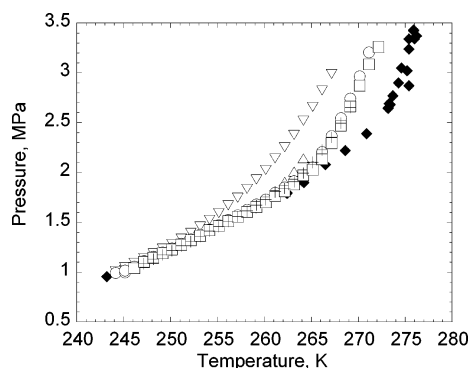
experiments was in good agreement with the total pore volume of the sample based on the pore volumes determined by nitrogen desorption studies.

As explained elsewhere (Wilder et al.<sup>5,11</sup>), because the silica gels each contained a broad distribution of pore sizes, it was insufficient to record only the equilibrium temperature and pressure for the data to be interpretable. Table 1 gives the total cell volume, including the volume due to the lines connecting the cell and those separated by valves. Headspace here denotes the space not occupied by either solid (silica gel, hydrate, and glass beads) or liquid (water inside pores of silica gel). The volumes of the silica gels were calculated based on their densities and the weights of silica gel used in each experiment. The volumes of the glass beads were measured by the rise of the water level in a measuring column after a known number of glass beads were added. The volume of each cell with connecting lines was determined by connecting each of them separately to a calibration cell with known volume.

Methane was simultaneously added to the five sample-filled cells at room temperature after the cells had been evacuated to remove impurity gases. Methane gas was charged to approximately 13.8 MPa in all of the cells as measured with a set of pressure transducers with a pressure range of 20.7 MPa. As indicated by the subsequent pressure drops in the cells, significant hydrate formation took place as the cell temperatures were brought down to 243 K. The samples were left for hydrate to form for 3 days. The pressures in each of the cells was then bled to a pressure slightly above the equilibrium pressure of bulk methane hydrate<sup>17</sup> at 243K, as measured by the smaller scale, more precise set of pressure transducers. At the same temperature, the gas pressure in each of the cells was further reduced to below the equilibrium pressure of bulk methane hydrate. The valves connecting the cells were then closed, isolating the samples. Pressures in each cell were then read over a period of around 1 to 3 days, until no further pressure changes were observed. After the lowest temperature point had been measured for each sample, the bath temperature was raised and the pressure in each cell again was read over a period of days until no further pressure changes were observed. The process of raising the bath temperature and reading the equilibrium pressures was repeated until substantially all of the hydrate was decomposed.

### Results and Discussion

Figure 1 is a plot of the experimental equilibrium pressures for methane hydrate decomposition in silica gels with nominal pore radii of 2.0, 3.0, 5.0, and 7.5 nm, or a mixture of 3.0 and 7.5 nm. Also shown are corresponding data from the literature (which are summarized in ref 17) for  $r$  equal to infinity, i.e., bulk methane hydrate. In regions where the equilibria involved



**Figure 1.** Experimental equilibrium pressures for methane hydrate in silica gels with nominal pore radii 2.0 nm (V), 3.0 nm (Δ), 5 nm (○), 7.5 nm (□), mixture of 3.0 and 7.5 nm (+), or infinity (◆); bulk hydrate data from Sloan.<sup>17</sup>

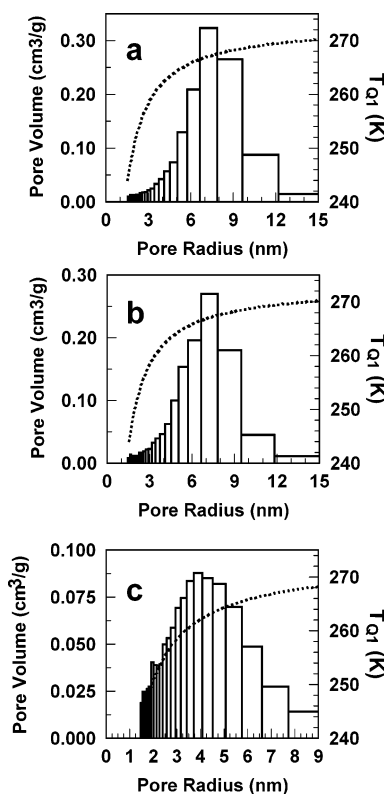
**TABLE 2: Pressure<sup>a</sup>–Temperature Data for Equilibria Involving Methane Hydrate in Silica Gel Pores of Various Nominal Radii**

<i>T</i> /K	<i>P</i> /MPa				
	2 nm	3 nm	5 nm	7.5 nm	50% 3 nm + 50% 7.5 nm <sup>b</sup>
244.2	1.012		0.992		
245.2	1.022		0.998		
245.2	1.050		1.017		
246.2	1.093		1.057	1.037	
247.2	1.142	1.090	1.115	1.104	1.085
248.2	1.188	1.134	1.155	1.145	1.130
249.2	1.235	1.178	1.198	1.188	1.174
250.2	1.283	1.216	1.239	1.229	1.217
251.2	1.338	1.265	1.286	1.276	1.266
252.2	1.396	1.310	1.330	1.319	1.309
253.2	1.458	1.358	1.376	1.365	1.357
254.2	1.525	1.415	1.429	1.421	1.413
255.2	1.593	1.460	1.472	1.462	1.458
256.2	1.671	1.516	1.524	1.510	1.508
257.2	1.748	1.571	1.572	1.556	1.558
258.2	1.836	1.635	1.626	1.604	1.614
259.2	1.931	1.690	1.680	1.655	1.672
260.2	2.027	1.739	1.730	1.700	1.728
261.2	2.142	1.812	1.797	1.764	1.805
262.2	2.253	1.906	1.851	1.812	1.844
263.2	2.377	2.009	1.912	1.880	1.906
264.2	2.521	2.142	1.969	1.972	1.994
265.2	2.659		2.051	2.028	2.103
266.2	2.824		2.206	2.132	2.228
267.2	2.989		2.366	2.294	2.355
268.2			2.545	2.471	2.495
269.2			2.743	2.663	2.653
270.2			2.966	2.872	
271.2			3.207	3.085	
272.2				3.261	

<sup>a</sup> Total measured pressure of gaseous methane and water. <sup>b</sup> The amount of water in the nominal 3 nm and 7.5 nm silica gels was the same.

liquid water (see below), the data exhibit the expected increase of equilibrium pressure with increasing values of  $1/r$ . The data plotted in Figure 1 are tabulated in Table 2. Note the close correspondence of the results for all of the silica gel samples and the bulk data at low temperatures (when the equilibria would be expected to involve ice). This range of correspondence varies from sample to sample due to the different pore-size distributions present in the various samples and the effect of pore size on the freezing point of water (see discussion below).

As reported elsewhere for ethane hydrate,<sup>6,11</sup> we note the close correspondence of the data for the silica gels with pores of nominal 7.5 and 5.0 nm radii up to a temperature of 269.2 K.



**Figure 2.** Quadruple point temperature,  $T_{Q1}(r)$  (dashed lines) and pore volume distributions based on the nitrogen desorption isotherms for silica gels with nominal pore radii of (a) 7.5, (b) 5.0, or (c) 3.0 nm.

Our previous work<sup>6</sup> showed the pore-volume distributions for these two media calculated (by the method described in ref 18) from nitrogen adsorption data; these distributions are presented in Figure 2. As can be seen, the two distributions are identical up to a pore radius of about 6 nm. Equilibria involving pores up to this size would lead to the close correspondence of the observed equilibrium pressures. From this we infer that below 269.2 K the equilibria are for radii smaller than 6 nm.

For the temperature range between 260.2 and 270.2 K, the equilibrium pressures measured for the mixed sample of nominal 3 and 7.5 nm silica gels are between those of the 3 nm sample and the 7.5 nm sample. At temperatures below this range, all of the samples had indistinguishable equilibrium pressures, while above 270.2 K the equilibrium pressures for the mixture were similar to those of the 7.5 nm sample. This suggests that the equilibria in the mixed sample at temperatures above 270.2 K corresponded to radii larger than any pore in the 3.0 nominal pore radius silica gel.

We have three goals for interpretation of the data in Table 2: (1) to discern which data are for the equilibrium of hydrate with liquid water and free methane gas and which data are for the equilibrium of hydrate with ice and free gas; (2) to compare the data for the hydrate/ice-plus-gas equilibrium in various sized pores with corresponding data for the bulk hydrate and show that there is no discernible difference; and (3) to compare the new data reported in this work with data in the literature.

**Determination of Equilibrium Type (Hydrate/Water or Hydrate/Ice).** Unlike a bulk hydrate that has a unique quadruple point, hydrate in a porous medium with a broad distribution of pore sizes does not have a single quadruple point. The pore-size distributions for the porous media used in this work were given in Figure 2, as determined<sup>18</sup> from measured nitrogen desorption isotherms. In Figure 2, the height of each vertical bar represents the pore volume for the pores having radii in the

range indicated by the width of the bar. For gases with negligible water solubilities, the quadruple point temperature is closely given by the melting point of water. As a result, the quadruple point temperature,  $T_{Q1}$ , for such hydrates is given by the freezing point of water in a cylindrical pore,<sup>19</sup> and can be expressed as a function of the pore radius,  $r$ :

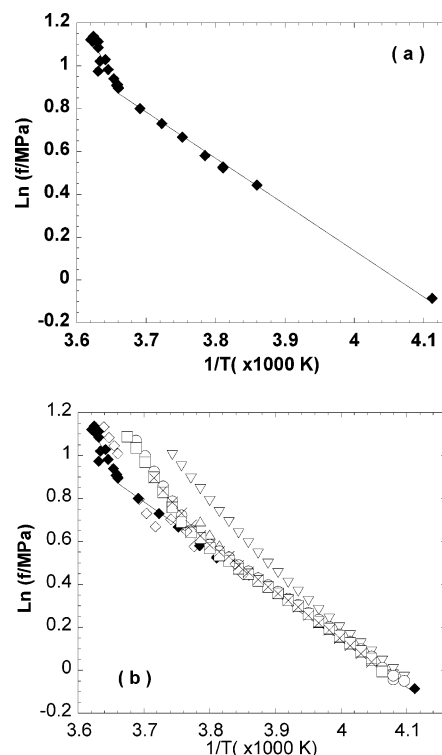
$$T_{Q1}(1/r) = T_{Q1}(0)(1 - 2\sigma/\rho\Delta Hr) \quad (1)$$

where  $T_{Q1}(0)$  is the quadruple point of bulk water (which, for hydrates formed from a gas with negligible water solubility is 273.2 K),  $\rho$  is the density of water (1000 kg/m<sup>3</sup>),  $\sigma$  is the surface tension (0.0267 J/m<sup>2</sup>) between water and ice,<sup>19</sup> and  $\Delta H$  is the specific enthalpy of fusion of bulk water (333 kJ/kg).<sup>20</sup> In eq 1 it is assumed that the capillary surface is a spherical cap. Other geometries would require a constant different from “2” in the numerator of the second term on the right-hand side. Plots of the quadruple point temperature for various pore radii calculated from eq 1 have been superposed on the distributions shown in Figure 2. Taken together, the plots shown in Figure 2 illustrate which pores of each hydrate–silica gel sample are above or below their  $T_{Q1}(1/r)$  at any given temperature.

Previous work<sup>12</sup> has shown that the van der Waals–Plaatouw equation for bulk hydrates (with a single guest component) leads to a relation for the logarithm of the equilibrium guest fugacity on either side of the quadruple point temperature which is linear in  $1/T$ :

$$\ln(f_i/\text{MPa}) = a_i + b_i/T \quad (2)$$

In eq 2,  $f_i$  is the guest fugacity, and  $a_i$  and  $b_i$  are constants which depend only on the guest species. Empirical relations of this or similar forms have previously been reported in the literature,<sup>17,21,22</sup> but prior to recent work<sup>12</sup> had not been shown to be derivable from a standard statistical thermodynamic model. Figure 3a contains a plot of  $\ln(f_i/\text{MPa})$  vs  $1/T$  for the bulk methane hydrate data of Figure 1 and a regression of eq 2 to the data. All of the fugacities presented in this work were calculated by using the Soave–Redlich–Kwong equation of state.<sup>23</sup> The values of  $a$ ,  $b$ , and the regression coefficient  $R$  for the regression in Figure 3a for the bulk data are listed in Table 3. It is apparent that eq 2 provides an excellent fit to the bulk data, and we anticipate that the published data for bulk methane hydrate will be an accurate basis for comparison of corresponding data for methane hydrate in pores. Figure 3b shows a similar plot for the experimental data reported in Table 2 and in Figure 1. Also shown are the bulk data lying in the indicated domain, and experimental data for porous glass of 15 nm nominal radius from Uchida et al.<sup>14</sup> Note that the data for each nominal pore size separate into two distinct segments. The segments which lie on top of the bulk ice–hydrate line presumably involve equilibria involving ice and hydrate in the respective silica gel pores. The data which lie above the bulk data would then correspond to equilibria involving liquid water and hydrate. On the basis of the evidence in Figure 3b, we have separated our data by classifying them as belonging to one of the two types of segments discussed above. In this manner we propose that in the experiments reported here, for the nominal 7.5 nm silica gel the data in Table 2 corresponding to temperatures less than or equal to 266.2 K were for equilibria involving hydrate and ice, while for the 5.0 nm and 3.0 nm silica gels only points corresponding to temperatures less than or equal to 265.2 and 252.2 K, respectively, involved ice. For the 2.0 nm silica gels, however, at most only the one or two points at the lowest temperatures likely involved hydrate–ice equilibrium. For the



**Figure 3.** Plots of  $\ln(f_i/\text{MPa})$  vs  $1/T$  of data in Figure 1 for (a) bulk methane hydrate and (b) pore hydrate in silica gels with nominal pore radii 2.0 nm ( $\nabla$ ), 3.0 nm ( $\Delta$ ), 5.0 nm ( $\circ$ ), 7.5 nm ( $\square$ ), mixture of 3.0 and 7.5 nm ( $+$ ), and in porous glass with nominal pore radius of 15 nm ( $\diamond$ ) (Uchida<sup>14</sup>) or infinity ( $\bullet$ ); bulk hydrate data from Sloan.<sup>17</sup>

**TABLE 3: Values of  $a_i$  and  $b_i$  in Eq 2**

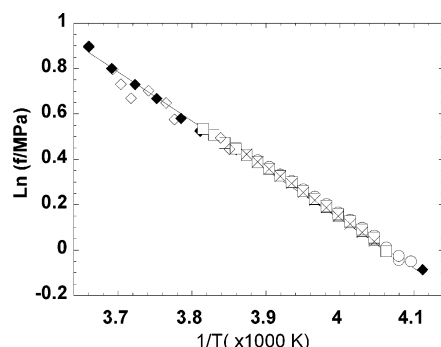
$r_i$	$a_i$	$b_i$ (K)	$R_i^a$	no. of data
3.0 nm	9.10	−2239.2	0.99987	11
5.0 nm	9.06	−2226.7	0.9984	15
7.5 nm	8.60	−2109.4	0.99886	17
mixture <sup>b</sup>	9.03	−2221.0	0.99983	12
infinite <sup>c</sup>	8.79	−2162.2	0.99799	10
av, this work	8.95	−2199.1	0.99924	55
av, all data	8.91	−2191.7	0.99899	65

<sup>a</sup> Regression coefficients. <sup>b</sup> 50% water in 3-nm pores and 50% water in 7.5-nm pores. <sup>c</sup> That is, bulk hydrate data presented by Sloan.<sup>17</sup>

mixture sample of 50% 3 nm and 50% 7.5 nm pore radii silica gel, points below 266.2 K involved ice. All of the other data in Table 2 correspond to equilibria involving hydrate and liquid water.

**Comparison of Bulk and Pore Data for Hydrate–Ice Equilibria.** Figure 4 is a plot of  $\ln(f_i/\text{MPa})$  vs  $1/T$  for methane hydrate in silica gels of various nominal pore sizes, along with the corresponding data for bulk methane hydrate. The temperature range of Figure 4 is restricted to the condition that  $T < T_{Q1}(1/r)$ , so that only data for the dissociation to free gas and ice are included. Also shown are regressions of the equation  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  to each set of data for the various silica gels. The values of  $a_i$  and  $b_i$  for the hydrate in the porous media are listed in Table 3. It is readily apparent from Figure 4 and Table 3 that for sufficiently low temperatures and the particular experimental procedure utilized here, there is little difference between the equilibrium pressures for the bulk hydrate and the pressures for the methane hydrate in the various porous media. In determining the fits in Table 3, data for the nominal 7.5 nm silica gel for temperatures less than or equal to 266.2 K from Table 2 were used, while for the 5.0 and 3.0 nm silica gels only points corresponding to temperatures less than or equal to





**Figure 4.** Plots of  $\ln(f/\text{MPa})$  vs  $1/T$  for bulk methane hydrate (taken from Sloan<sup>17</sup>) and for methane hydrate in silica gels with nominal pore radii 2.0 nm (▼), 3.0 nm (Δ), 5.0 nm (○), 7.5 nm (□), mixture of 3.0 and 7.5 nm (+), and in porous glass with nominal pore radius of 15 nm (◇) (Uchida<sup>14</sup>), for temperatures below  $T_{Q1}(1/r)$ , of the smallest radius pores in which hydrate formed.

265.2 and 252.2 K, respectively, were used. In addition, a fit of eq 2 to all of the data for methane hydrate in pores (dotted trace) is shown in the figure, though it is indistinguishable from the regression lines for the bulk data, or from the regressions for the individual sets of data. The results shown in Table 3 clearly indicate that for sufficiently low-temperature ranges there were no detectable differences between the observed equilibrium pressures for methane hydrates in various size silica gel pores and the equilibrium pressures for the bulk hydrate at the same temperatures. The specifics of the various regressions performed to construct Table 3 are as follows:

As listed in Table 3, for 10 points for the bulk hydrate the value of  $a_i$  was 8.79; for the porous media the values of  $a_i$  were 8.60 (17 points), 9.06 (15 points), and 9.10 (11 points), respectively, for the nominal 7.5, 5.0, and 3.0 nm porous media. For the mixed porous media made of 3.0 and 7.5 nm silica gel, the value for  $a_i$  was 8.79 (12 points). For all 55 points for the porous media the value of  $a_i = 8.95$ , compared to  $a_i = 8.79$  for the 10 bulk hydrate data points. For the various porous media the values of  $b_i$  ranged from  $-2109$  to  $-2239$ , with  $b_i = -2199$  for all of the porous-media data considered as a single group; these values may be compared to  $-2192$  for the bulk hydrate. There may be a systematic variation in  $a_i$  and  $b_i$  with average pore size, but any such variation, if present, is very small and may be due to a systematic error in reading the equilibrium pressure at lower temperatures where the smallness of the pressure could lead to larger relative errors. The consistency in the values of  $a_i$  and  $b_i$  for these various regressions strongly suggests that the results for the pore hydrates are indistinguishable from the bulk results over the temperature ranges indicated above.

**Interpretation of Low-Temperature Data.** Earlier experimental results<sup>2</sup> for methane hydrates in 7 nm nominal radius silica gels showed equilibrium pressures above those for the bulk for all of the temperatures at which pressures were measured. The lowest temperature for which Handa and Stupin report the equilibrium pressure for methane hydrate in this porous medium is 263 K. Use of eq 2 indicates that at 263 K hydrate in all pores having radii smaller than 4.4 nm would dissociate to methane and liquid water. According to our nitrogen desorption and other studies,<sup>5,11</sup> such pores represent 34.5% of the total pore volume of a similar medium. Since the equilibrium pressure for the smallest pores would be greater than that for larger pores, the first measured equilibrium pressure would correspond to that for the smallest hydrate-containing pores in the sample. Thus, at 263 K the equilibria for the smallest 34.5 vol % of the pores involve liquid water. Therefore, we

believe the data reported by Handa and Stupin starting at 263 K represent equilibria between hydrate and free gas + liquid water. We note that Handa and Stupin observed a slight change in the slope of a plot of  $\log(\text{fugacity})$  versus reciprocal temperature based on their experimental data. They interpreted this to represent the transition from equilibria involving ice to equilibria involving liquid water, as would be correct for bulk measurements, or for those in a medium containing only a single pore size. However, in media containing a distribution of pore sizes, each measured equilibrium pressure may correspond to a different size pore.<sup>5</sup> In this case, one is in fact moving along a curve on a surface where  $\log(\text{fugacity})$  depends on the reciprocal of the pore size as well as the reciprocal temperature.<sup>12</sup> Since the pore size involved in the equilibria changes as the temperature is raised, the changes in the slope of the  $\log(\text{fugacity})$  versus reciprocal temperature plot of their experimental data may be due either to a phase change of the water or to a change in the slope of the pore volume distribution as a function of pore radius (as illustrated by Figure 2a). (Each time the temperature was raised, hydrate dissociated in successively larger pores until sufficient gas was released into the headspace to reach the new equilibrium pressure—which depends on the final pore size as well as the final temperature. Thus we conjecture that the apparent change of slope in the  $\log(\text{fugacity})$  versus reciprocal temperature plot may correspond to the temperature at which the pore size of the equilibrium equaled the maximum in the pore size distribution.)

This conjecture may or may not be correct; the important point is that because of the distribution of pore sizes present in their sample, there was no unique quadruple point temperature and the data cannot be interpreted in terms of two enthalpies (one for above and one for below a unique quadruple point). Our data (Figure 4) seem to show that the heat of dissociation of hydrate to methane and ice is the same for the hydrate in the pores as in the bulk; the data of Handa and Stupin indicate that the former heat is smaller. We can only conclude that any difference was too small for us to detect, and that unfortunately no conclusions about this question can be drawn from the earlier work.

We started our experiments at a temperature (243 K) that was 10 K below that used by Handa and Stupin.<sup>2</sup> Equation 1 predicts that only pores with radii less than 1.4 nm would contain liquid water at this temperature. As can be seen in Figure 2 of our previous work (Zhang et al.<sup>6</sup>), there is no measurable volume in pores with radii less than 1.4 nm. Therefore, our data do include equilibria involving hydrate and free gas + ice, since there were no hydrate containing pores for which the equilibria would have involved liquid water at 243 K. We believe that the interaction of the pore size distribution with the smallness of this initial experimental temperature allowed us to obtain data for hydrate formation in this porous medium involving ice as well as other (higher temperature) data where it involved liquid water.

We believe that Figure 4 strongly suggests that for equilibria involving ice, there is no detectable difference between the equilibrium pressures for methane hydrate formation in silica gel pores and those in the bulk. As is clear in Figures 1 and 3b, at higher temperatures (where the equilibrium involves liquid water), there is an increase in the equilibrium pressure for hydrates in the silica gel pores. As discussed elsewhere,<sup>6</sup> there are several other possible explanations for the correspondence of the low-temperature pore data with the bulk data. However, as discussed in detail in this previous work,<sup>6</sup> there is currently no experimental evidence to support these more complex

explanations. In addition, all of the relevant data in the literature (those in the current work as well as data found in Zhang et al.<sup>6</sup> and Uchida et al.<sup>14</sup>) seem to support our simpler conclusion that there are no observable pore size effects on the equilibrium pressure when the equilibrium involves ice. To better resolve this issue, more conclusive experimental evidence needs to be presented that either confirms or refutes our simple explanation.

The implications of our model for hydrate equilibria in porous media include<sup>5,8</sup> the following: (1) the product  $\sigma \cos(\theta)$  (the surface tension times the cosine of the contact angle) for equilibria involving liquid water and hydrate can be approximated by that between liquid water and ice (0.0267 J/m<sup>2</sup>), and (2) that for equilibria between ice and hydrate,  $\sigma \cos(\theta)$ , is sufficiently small to be approximated as zero.

To test the first of these implications, pore volume distributions have been constructed from data for hydrate–liquid water equilibria and compared to those obtained from nitrogen desorption studies.<sup>5,8</sup> These comparisons have shown very good agreement, suggesting that for the hydrate–liquid water equilibrium the value of  $\sigma \cos(\theta)$  can be approximated as 0.0267 J/m<sup>2</sup>, although best-fits to various sets of hydrate data may give values that are somewhat smaller or larger.

As discussed above, this work, our previous work on ethane hydrate,<sup>6</sup> and the data for methane hydrate in 15 nm (radii) porous glass reported by Uchida et al.<sup>14</sup> all contain data for hydrate equilibria in porous media where the equilibria involve ice. (The latter data also are plotted in Figures 2 and 3, as open diamonds.) All of these studies found equilibrium pressures that agree with those observed in the corresponding bulk hydrate, regardless of the size of the pore in which the hydrate resides when the equilibrium involved ice. We note that Uchida et al.<sup>14</sup> state that “Although the experimental results obtained in the present study look as if they support their [Wilder et al.<sup>5</sup>] prediction, we consider the interfacial tension between ice and hydrate to not be zero as discussed above. Further experimental efforts and discussions are required to clarify the nature of the equilibrium conditions of gas hydrates in small pores below the quadruple point” (parenthetical reference added for clarity). In order for the equilibrium pressures observed in porous media to agree with those for bulk hydrates, the term related to the capillary pressure effects on the hydrate equilibrium must be negligible. This term involves the product  $\sigma \cos(\theta)$ , the reciprocal of the pore radius, and several physical constants (see refs 1 and 19). For a porous medium, the reciprocal of the pore radius is obviously different from zero. The agreement of experimental pore hydrate equilibrium pressures with bulk equilibrium pressures when the equilibria involve ice therefore suggests that the product  $\sigma \cos(\theta)$  is very small when the equilibrium involves ice, thus supporting the second hypothesis given above, namely that  $\sigma \cos(\theta)$  is not significantly different from zero when the equilibrium involves ice.

The smallness of the product  $\sigma \cos(\theta)$  implies that either  $\sigma$  or  $\cos(\theta)$  (or both) is (are) negligible. Uchida et al.<sup>14</sup> have proposed the value of 0.041 J/m<sup>2</sup> for the surface energy between hydrate and ice, based on previous results involving the examination of air hydrate crystals trapped along ice grain boundaries.<sup>24</sup> Accepting this value for the surface energy between ice and hydrate, we are left to conclude that the smallness of the product  $\sigma \cos(\theta)$  must be due to the contact angle being approximately 90° (making  $\cos(\theta)$  negligible).

## Summary

We have previously proposed that the dissociation of hydrate to ice and free gas in porous media should be independent of

pore size, and that the associated equilibrium pressures should agree with those observed for the bulk. This prediction was recently supported by the data of Uchida et al.<sup>14</sup> for methane hydrate in porous glass with nominal pore radii of 15 nm, and by the data of Zhang et al.<sup>6,7</sup> for ethane hydrate in porous silica gel with nominal pore radii of 3.0, 5.0, and 7.5 nm. We have here presented equilibrium pressure data for methane hydrates in silica gel pores with nominal radii of 2.0, 3.0, 5.0, and 7.5 nm and a mixture of 3.0 and 7.5 nm silica gels. The data for equilibria involving ice are in excellent agreement with previous results for bulk methane hydrates (summarized in Sloan<sup>17</sup>). This result supports our previous hypothesis<sup>5–7,11</sup> that there is no detectable surface stress affect between hydrate and ice, suggesting that  $\sigma \cos(\theta)$  is sufficiently small so as to be negligible. On the basis of current and previous work, we believe that for equilibria involving free gas, ice, and a single guest component hydrate, the equilibrium pressure is independent of pore size, and is indistinguishable from the equilibrium pressure for the bulk hydrate at the corresponding temperature.

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