

# Equilibrium Pressures and Temperatures for Equilibria Involving Hydrate, Ice, and Free Gas in Porous Media

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Equilibrium pressures for the dissociation of hydrate confined in silica gel pores of nominal radii 7.5, 5.0, or 3.0 nm were measured of a range of temperatures for methane and ethane hydrates. Each of these porous media contained a broad distribution of pore radii. As reported elsewhere, at higher temperatures the pressures were larger than the pressures previously reported for the bulk hydrate. This behavior is observed when the hydrate dissociates to liquid water. Because the quadruple point temperature depends on pore size, this behavior occurs when the experimental temperature is above the quadruple point temperature for the size pore involved in the equilibrium. It now appears that the van der Waals-Platteeuw equation for bulk hydrates, when modified to include the capillary pressure effect of the pores, can be used to interpret these results. This model predicts that at sufficiently low temperatures, below the quadruple point temperature of the smallest hydrate-containing pore, there should be little effect of pore size on the equilibrium pressures. We have subjected this prediction to experimental tests, by measuring the equilibrium pressures at low temperatures. We found that at the lowest temperatures, where the equilibria involved ice, the pressures were identical (within expected experimental uncertainties) for all three silica gels. Furthermore, the pressures for the various porous media were the same as reported by others for the bulk hydrate. This behavior at the lowest temperatures indicates that there was no significant capillary pressure effect below the quadruple point temperature of the smallest pore in which hydrate formed. The experimental results suggest two conclusions for the model: (1) that for both equilibria, involving either solid or liquid water, the interface relevant to the formation of hydrate in silica gel pores is that between the hydrate and the aqueous phase (as suggested by Henry et al., 1999, Uchida et al, 1999, and others); and (2) that within experimental error, the surface energy between the hydrate and water (either liquid or solid) can be approximated by that between ice and the appropriate aqueous phase. Thus, when the temperature is relatively high and the equilibrium involves liquid water, the operative interfacial tension is between hydrate and liquid water, this tension is very close to the tension between ice and liquid water, and the pore effect can be quite large. However, when the temperature is sufficiently low that the equilibrium involves solid water, the operative interfacial tension is between hydrate and ice, and this tension is very close to zero. Then, the capillary pressure effect is very small; and the equilibrium pressure is essentially the same for all pore sizes, including infinity (i.e., the bulk hydrate).

## 1 Introduction

Clathrate hydrates are solids in which some of the cages formed by the hydrogen-bonded water molecules making up the hydrate lattice are occupied by a small guest-species molecule. Hydrates are formed by methane, ethane, propane, carbon dioxide, hydrogen sulfide, and other components of natural gas. Long studied because they can form in pipelines and block the flow of gas, natural gas hydrates also form in the earth's crust in arctic regions and beneath the seafloor around the margins of most continental shelves. Because of increased drilling in the arctic and in deep ocean waters, natural gas hydrates now are of considerable interest for problems they might cause during the drilling and production for oil or "conventional" natural gas, and also because they represent a potentially huge source of fuel (often estimated to be larger than all other sources of fossil fuel combined (Sloan, 1997)).

Although hydrates can occur naturally as small nodules of "bulk" material, more often they are dispersed throughout the pores of terrestrial or sub-seafloor

sediments (Sloan, 1997). The occurrence of hydrate deposits in porous media has motivated both experimental (Handa and Stupin, 1992; Uchida et al, 1999; Seshadri et al, 2001) and modeling studies (Clark et al, 1999; Henry and Clennell, 1999) of the effects of pore size on the thermodynamics of hydrate formation and dissociation. Several authors of modeling studies have concurred that the thermodynamics of hydrates in porous media should be described by the van der Waals-Platteeuw equation (van der Waals and Platteeuw, 1959) 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. To date, both the experimental and theoretical studies have primarily focused on the decomposition of hydrates in porous media to liquid water. Two different ideas for the identity of the capillary interface, and thus for the value of the interfacial tension in the capillary pressure term, have been suggested. However, neither value for the tension gave satisfactory agreement (Clarke

et al, 1999; Henry and Clennell, 1999) of the modified van der Waals-Plaateuw equation with the experimental data (Handa and Stupin, 1992). This lack of agreement has been attributed (Wilder et al, 2001a) to the use (Clarke et al, 1999; Henry and Clennell, 1999) of a single value for the pore radius in the predictive equation, even though the porous medium contained a broad range of pore radii (Handa and Stupin, 1992).

Since the porous media contain various size pores, we propose that each experimental point ( $P, T$ ) measures the hydrate formation-dissociation equilibrium in a different size pore: what appears to be a line in two-dimensional  $P$ - $T$  space is actually a line across a  $P$ - $T$ - $r$  surface. For most hydrates, the values of all of the parameters in the van der Waals-Plaateuw equation are known; hence, in the modified equation for hydrates in pores, only the values of  $r$  (the pore radius),  $\sigma$  (the interfacial tension), and  $\cos \theta$  (cosine of the contact angle) are uncertain. Hence, if the value of  $\sigma \cos(\theta)$  can be deduced, the value of  $r$  unique to each value of  $P$  and  $T$  can be calculated from the measured  $P$  and  $T$  and the van der Waals-Plaateuw equation. Work by our group (Wilder, 2001a) has shown that when the equilibrium is for the dissociation of hydrate to free gas and liquid water, and the correct value of the tension is assumed to be very close to that between liquid and solid water, the pore size distributions obtained in this way agree very well with pore size distributions obtained from nitrogen desorption isotherms. (The tension used follows from the hypotheses that the operative surface is between hydrate and liquid water, and that this tension is nearly equal to the tension between ice and liquid water (Henry and Clennell, 1992).)

Questions of the relevant interface and the correct value for the surface tension have been discussed in several studies. The calculations of Clarke et al. (1999) (where the authors assumed a gas/water interface and used a surface tension of  $0.072 \text{ J/m}^2$ ) show definite, significant differences between equilibrium pressures in porous media and those in the bulk when the equilibrium involves ice (see Figs. 3 and 4 of Clarke et al, 1999). Henry et al. (1999) assumed that the relevant interface was between the hydrate and aqueous phases, and used a value of  $0.0267 \text{ J/m}^2$  for equilibria involving liquid water.<sup>a</sup> The calculations of Henry et al. (1999) 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 (1999) suggest 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 the surface tension between hydrate and liquid water is nearly that between ice and liquid water, the surface energy effects between hydrate and ice should be very

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<sup>a</sup> We note that Klauda and Sandler (2001) present a method for calculation of hydrate equilibrium pressures in porous media based on a different method, but use the same interface and interfacial tension as Henry et al. (1999).

small. As a result, we propose that at any temperature below its quadruple point, the equilibrium pressure for any size pore should be the same as for the bulk at that temperature. Hence, in media with a distribution of pore sizes, if 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 for the bulk. This paper presents experimental results for methane or ethane hydrate equilibria in silica gels of different pore-size distributions that support this hypothesis. As discussed below, the quadruple point temperature decreases with decreasing pore size. The experimental data are used to test the prediction 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.

## 2 Experimental Methods

A multiple cell system was used to allow for the simultaneous measurement of the equilibrium pressures for three different samples of silica gel. The system consisted of 3 individual cells, similar to those that have previously been described in the literature (Seshadri et al, 2001), and which were connected to the same gas inlet via valves. The cells were independent of each other in terms of the cell pressure, but were immersed in the same temperature controlled bath. All three cells were of identical geometry. The working pressure of the multiple cell system was up to 13.6MPa. The volume of each cell and its connecting tubes and valves ranged from 68.1 to 68.7 cm<sup>3</sup>.

The silica gel samples, without any further treatment, were placed in a desiccator containing degassed, distilled water for a period of about 7 days to prepare silica gel with sorbed water. The silica gel powder for each cell was mixed with 5-mm-diameter glass beads, and loaded into the cells. The preparation of the hydrates and the subsequent determination of the equilibrium pressure-temperature profiles for their dissociation were performed in a manner similar to that used previously by Handa and Stupin (1992) for methane and propane hydrates in a silica gel with nominal 7 nm pores, and by Seshadri et al. (2001) for propane hydrate in the three silica gels used in this work.

## 3 Results and Discussion

Figure 1 shows the pore-volume distributions for the silica gels used in this work based on nitrogen desorption studies using Quantachrome Corp Autosorb-1 equipment.

Figure 2 is a plot of the experimental equilibrium pressures for ethane hydrate decomposition in silica gels with nominal pore radii of 3.0, 5.0, or 7.5 nm. Also shown are corresponding data from the

literature (Sloan, 1997) for  $r$  equal to infinity, i.e., bulk ethane hydrate. In general, the data qualitatively exhibit the expected increase of equilibrium pressure with increasing values of  $1/r$ . 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).

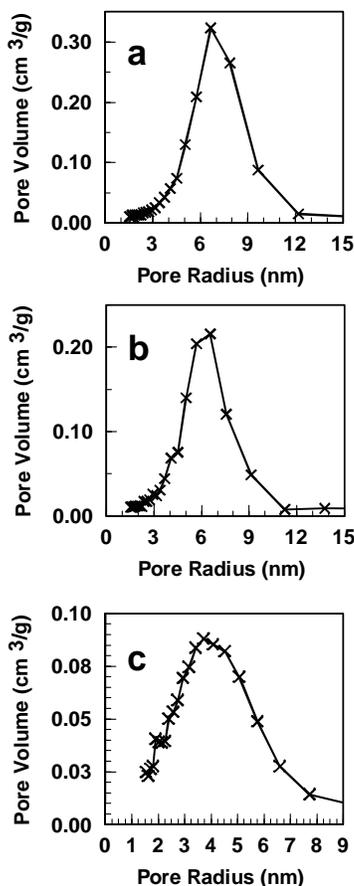


Fig. 1 Pore volume distributions based on the nitrogen desorption isotherms for silica gels with nominal pore radii of (a) 7.5, (b) 5.0, or (c) 3.0 nm.

Figure 3 shows the experimental data for methane hydrate equilibria in nominal 5.0 or 7.5 nm silica gel pores, as well as the experimental data from Sloan (1997) for bulk hydrate.

We have two goals for interpretation of the data in Figures 2 and 3: (1) to discern which data are for the equilibrium of hydrate with liquid water and free gas and which data are for the equilibrium of hydrate with ice and free gas; and (2) to compare the data for the

hydrate/ice-plus-gas equilibrium in various sized pores with corresponding data for the bulk hydrate.

As shown elsewhere (Wilder et al, 2001), the usual treatment of the van der Waals-Plaatuw equation predicts that, except for very small higher-order terms, for bulk hydrates (with a single guest component) the logarithm of the equilibrium guest fugacity on either side

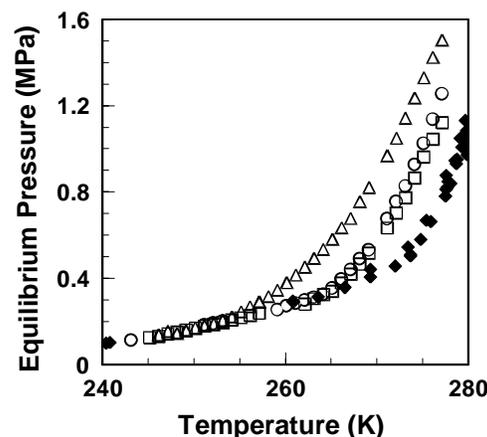


Fig. 2: Experimentally measured equilibrium pressures in silica gels of nominal pore radii 7.5 (□), 5 (○), or 3 (△) nm for ethane hydrate. Also shown are results from the literature for bulk hydrate formation (◆).

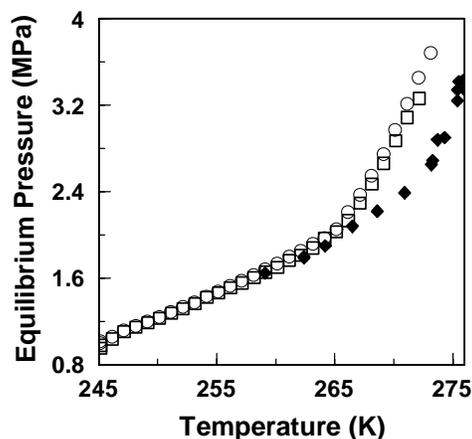


Fig. 3: Experimentally measured equilibrium pressures in silica gels of nominal pore radii 7.5 (□) or 5 (○) nm for methane hydrate. Also shown are results for bulk hydrate formation (◆).

of the quadruple point temperature should be a linear function of  $1/T$ :

$$\ln(f/\text{MPa}) = a_i + b_i/T \quad (1)$$

Empirical relations of this or similar forms have

previously been reported in the literature (Sloan, 1997; Kamath, 1984), but prior to recent work (Wilder et al, 2001) had not been shown to be derivable from a standard statistical thermodynamic model.

Comparisons of data for bulk hydrate and for hydrate in pores must be for the same equilibrium. While a bulk hydrate has a unique quadruple point, the hydrate in a porous medium with a broad distribution of pore sizes does not. For gases with negligible water solubilities, the quadruple point temperature is closely given by the melting point of water. Since the effect of a restricted geometry on the melting point of a pure substance is well known, the quadruple point temperature,  $T_{Q1}$ , can be expressed (Clennell et al, 1999) as a function of the pore radius,  $r$ :

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

where  $T_{Q1}(0)$  is the quadruple point of bulk water (which, for hydrates formed from a gas with negligible water solubility is 273.15 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 (Henry and Clennell, 1999), and  $\Delta H$  is the specific enthalpy of fusion of bulk water (333 kJ/kg). Due to the pore-volume distribution present in the silica gel samples used in this work (see Fig. 1), part of the pores in the sample will contain liquid water, while the rest will contain ice for experimental temperatures in between the quadruple point for the largest size pore present in the sample and that for the smallest size. Only if one is below the quadruple point temperature for the smallest pore filled with water will all of the pores contain ice. When one considers hydrate equilibrium measurements the question of the state of the water involved in the equilibrium is complicated by the fact that the size pore involved in the equilibrium changes as the experiment progresses (see Wilder et al, 2001a).

Figure 4 contains a summary plot of  $\ln(f_i/\text{MPa})$  vs.  $1/T$  for bulk ethane hydrate and for ethane hydrate in silica gels of nominal pore radii 7.5, 5.0, and 3.0 nm, as well as fits of eq 1 to (i) the bulk ethane hydrate data (solid trace) and (ii) all of the data for ethane hydrate in pores (dotted trace). The temperature range of Fig. 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 obtained here are regressions of the equation  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  to each set of data. The values of  $a_i$  and  $b_i$  for the hydrate in the porous medium also are listed in Table 1. Note that the various regressions in Fig. 4 are indistinguishable. It is readily apparent from Figure 4 and Table 1 that for the particular experimental procedure utilized here there is little difference between the equilibrium pressures for the bulk hydrate and the pressures for the ethane hydrate in the various size silica gels for temperatures below 266.15K.

Figure 4 of this work strongly suggests that, when the equilibrium involves ice, there is no detectable difference between the equilibrium pressures for ethane

hydrate formation in silica gel pores with a nominal pore radius of 7.5 nm and those in the bulk. As is clear in Fig. 2, at higher temperatures (where the equilibrium would

**Table 1:** Values of  $a_i$  and  $b_i$  in  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  for ethane hydrate in silica gel pores of various nominal radii.

$r_i$	$a_i$	$b_i(\text{K})$	${}^aR_i$	$N$
3.0 nm	10.26	-3018	0.9525	7
5.0 nm	10.59	-3101	0.9971	11
7.5 nm	10.64	-3116	0.9971	19
infinity <sup>b</sup>	10.52	-3084	0.9996	12
ave., this work	10.57	-3096	0.9966	37

<sup>a</sup> regression coefficient  
<sup>b</sup> ie., bulk hydrate

involve liquid water), there is a significant increase in the equilibrium pressure for hydrates in the silica gel pores. This demonstrates (1) that there was hydrate in the pores (thus removing the question of whether the correspondence discussed above between the pore and bulk hydrate equilibrium pressures might be due to the presence of bulk hydrate and the absence of pore hydrate); and (2) that the magnitude of the effect of the

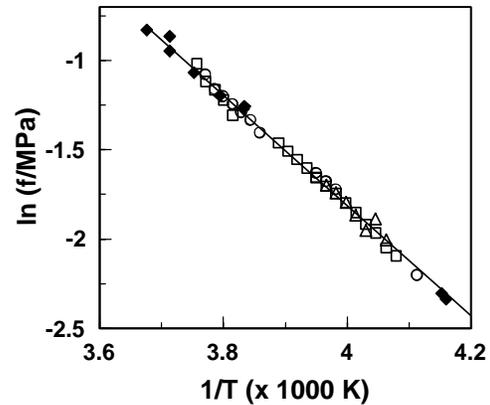


Fig. 4 Plots of  $\ln(f_i/\text{MPa})$  vs.  $1/T$  for bulk (◆) ethane hydrate and for ethane hydrate in silica gels of nominal pore radii 3.0 (△), 5.0 (○), or 7.5 (□) nm, for temperatures below  $T_{Q1}(r)$  of the smallest-radius pores in which hydrate formed. Note that the regressions of the equation  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  to the bulk (solid trace) and pore (dotted trace) data are indistinguishable.

restricted geometry at this nominal pore size (removing the question of whether pore effects are significant for ethane hydrates at this nominal pore size).

Further support for the conclusion that there is almost no dependence of the equilibrium pressure on

pore size when the equilibrium involves ice is provided by the data for ethane hydrate in silica gels with other pore-size distributions. Equation 1 also has been fit to measurements with silica gel of 3.0 nm or 5.0 nm nominal pore radius. The resulting values of  $a_i$  and  $b_i$ , as well as the number of points used in each fit, are listed in Table 1.

As listed in Table 1, for 12 points for the bulk hydrate the value of  $a_i$  was 10.52; for the porous media the values of  $a_i$  were 10.64 (19 points), 10.59 (11 points), and 10.26 (7 points), respectively, for the nominal 7.5, 5.0, and 3.0 nm porous media. For all 37 points for the porous media the value of  $a_i = 10.57$ , compared to  $a_i = 10.52$  for the 12 bulk hydrate data.

For the various porous media the values of  $b_i$  ranged from -3018 to -3116, with  $b_i = -3096$  for all of the porous-media data considered as a single group; these values may be compared to -3084 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.

Figure 5 contains a summary plot of  $\ln(f_i/\text{MPa})$  vs.  $1/T$  for bulk methane hydrate and for methane hydrate in silica gels of nominal pore radii 7.5 or 5.0 nm, as well as fits of eq 1 to (i) the bulk methane hydrate data (solid trace) and (ii) all of the data for methane hydrate in pores (dotted trace). As done in Fig. 4, the temperature range of Fig. 5 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. The values of  $a_i$  and  $b_i$  for all of the hydrate samples are listed in Table 2. It is readily apparent from Fig 5 that there is little difference between the equilibrium pressures for the bulk hydrate and the pressures for the methane hydrate in these size silica gels over the examined temperature range. Examination of Table 2 shows that there is a variation in  $a_i$  and  $b_i$  of only about 1% when the pore data are compared with the values for bulk methane hydrate, implying that the differences between these results for pore hydrate and the previously reported bulk data are less than experimental uncertainty.

#### 4 Conclusions

One consequence of the assumption that the interfacial tension between liquid water and hydrate can be approximated as that between liquid water and ice is the prediction that there should be negligible pore size effects on the equilibrium pressure when the equilibrium involves ice. This work has presented equilibrium pressure data for methane or ethane hydrates in silica gel pores with various nominal radii. While data in the liquid-water region showed the

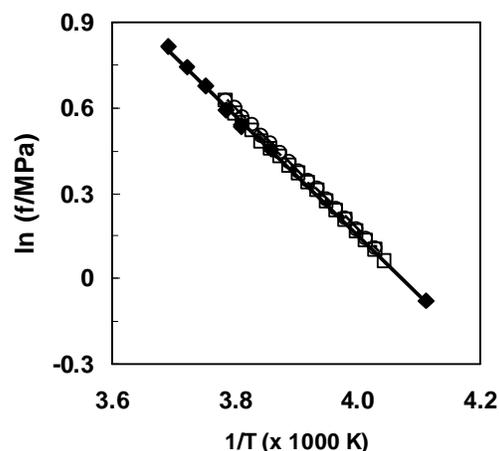


Fig. 5 Plots of  $\ln(f_i/\text{MPa})$  vs.  $1/T$  for bulk ( $\blacklozenge$ ) methane hydrate and for methane hydrate in silica gels of nominal pore radii 5.0 ( $\circ$ ) or 7.5 ( $\square$ ) nm, for temperatures below  $T_{Q1}(r)$  of the smallest-radius pores in which hydrate formed. Note that the regressions of the equation  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  to the bulk (solid trace) and pore (dotted trace) data are indistinguishable.

**Table 2:** Values of  $a_i$  and  $b_i$  in  $\ln(f_i/\text{MPa}) = a_i + b_i/T$  for methane hydrate in silica gel pores of various nominal radii.

$r_i$	$a_i$	$b_i(\text{K})$	$^a R_i$	N
5.0 nm	8.675	-2126	0.9999	17
7.5 nm	8.570	-2102	0.9995	18
infinity <sup>b</sup>	8.583	-2108	0.9992	7
ave., this work	8.631	-2116	0.9992	35

<sup>a</sup> regression coefficient

<sup>b</sup> ie., bulk hydrate

expected dependence on pore radius, the data for equilibria involving ice showed no dependence on pore radius, and they are in excellent agreement with previous results for bulk hydrates (Sloan, 1997). This result suggests that there is no detectable surface stress between the hydrate and ice. This result further supports the use of  $0.0267 \text{ J/m}^2$  to approximate the interfacial tension between hydrate and liquid water. In summary, we conclude that for the equilibrium of methane or ethane hydrate with ice and free gas the equilibrium pressure was independent of pore size, and was indistinguishable from the equilibrium pressure for bulk hydrate at the corresponding temperature.

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