

## Characteristics of Clathrate Hydrate Equilibria in Mesopores and Interpretation of Experimental Data

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The characteristics of clathrate hydrate equilibria in mesoporous media are discussed in terms of a conceptual model, with the aim of resolving current inconsistencies concerning experimental and interpretative methods employed in studies of such systems. This conceptual model is used as the basis for an analysis of experimental results from our own work and that of others. From this review, we conclude the following: (1) the Gibbs–Thomson (or Kelvin) relationship used to model clathrate inhibition in porous media must be modified correctly to reflect the hysteresis between growth and dissociation; (2) step heating provides more-reliable data than continuous heating techniques; (3) if equilibrium dissociation data cover the complete pore size distribution, then, contrary to what has previously been proposed by some researchers, inhibition can be interpreted in terms of the mean pore diameter; and (4) the enthalpy of clathrate dissociation is not a strong function of pore size (crystal size), as has been suggested in other studies.

### Introduction

Handa and Stupin<sup>1</sup> were the first to measure clathrate (or hydrate) inhibition (reduction of thermodynamic stability to lower temperatures or higher pressures, with respect to bulk conditions) of methane and propane clathrates in mesoporous silica, which they attributed to capillary-pressure-induced depression of the water activity. More recently, Uchida et al.<sup>2,3</sup> presented experimental ice melting and clathrate dissociation data for methane, carbon dioxide, and propane hydrates in porous silica, and, using the Gibbs–Thomson (or Kelvin) relationship detailed by Clennell et al.<sup>4</sup> and Henry et al.,<sup>5</sup> calculated values for ice–liquid and clathrate–liquid interfacial tensions.

In a series of publications, Wilder et al.,<sup>6</sup> Seshradi et al.,<sup>7</sup> Smith et al.,<sup>8,9</sup> and Zhang et al.<sup>10</sup> employed a *PTVr* (pressure–temperature–volume–pore radius) conceptual model to explain the apparent increased degrees of freedom associated with clathrate equilibria in mesoporous media with a pore size distribution. These authors concluded (or assumed) that the mean pore diameter could not be used to interpret experimental equilibrium data and, instead, used a capillary-modified (according to the equation detailed by Clennell et al.<sup>4</sup>) statistical thermodynamic model to calculate pore radii for their experimental measurements.

From a review of available literature,<sup>1–3,6–10</sup> it appears that opinion varies considerably as to which experimental methods should be used to measure clathrate equilibria in porous media and how data should be interpreted. Several workers have favored continuous heating methods,<sup>2,3</sup> while others have employed step-heating techniques for data generation.<sup>1,6–10</sup> Regarding data interpretation, dissociation conditions have been interpreted by some authors in terms of the mean pore diameter,<sup>2,3</sup> directly contradicting proposals by others that this is not possible.<sup>6–10</sup> Furthermore, it appears that there is a

common misunderstanding concerning the appropriate Gibbs–Thomson equation that should be used to describe the relationship between clathrate dissociation temperature depression and pore size. The majority of workers to date have employed the equation detailed in the conceptual model of Clennell et al.<sup>4</sup> and Henry et al.<sup>5</sup> However, this relationship describes clathrate *growth* in porous media, not dissociation, which is represented by the published experimental hydrate data.

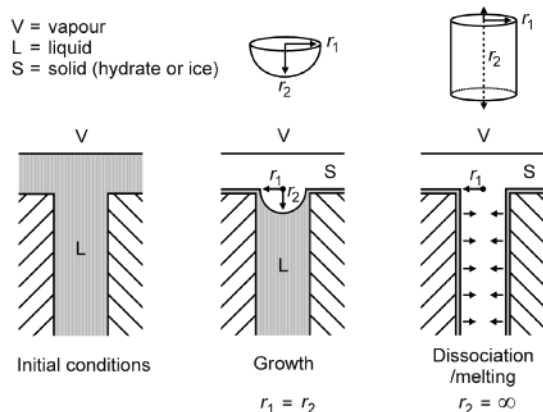
A final point of interest concerns the enthalpy of hydrate dissociation ( $\Delta H_{h,d}$ ) in porous media—an important factor in the Gibbs–Thomson equation. It has been suggested that the specific enthalpy of dissociation depends on pore size; the value of  $\Delta H_{h,d}$  apparently decreases as the pore diameter decreases.<sup>1,7</sup> If this were true, it would affect the thermodynamic calculations of clathrate stability in porous media; thus, the issue requires clarification.

In a companion paper to this work,<sup>11</sup> we present the results of an experimental study of structure-I (methane and carbon dioxide) clathrate hydrate equilibria in mesoporous silica. The aim of this paper is to clarify clathrate dissociation behavior in mesoporous materials, with respect to pore size distribution, and to resolve contradictions concerning the measurement and interpretation of experimental data for such systems. We first address the characteristics of hydrate equilibria in porous media, with respect to thermodynamic constraints, and then propose a simple conceptual model to explain observed dissociation behavior. Experimental results from our own work and that of others are then discussed, with respect to this model.

### Thermodynamic Constraints on Clathrate Dissociation in Porous Media

In a porous medium saturated with liquid (liquid volume greater than or equal to pore volume), clathrate growth/dissociation inhibition (or water melting/freezing point depression) results from an increased equilibrium pressure in the solid phase induced by the high curvature of the solid–liquid

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**Figure 1.** Illustration of the different solid–liquid interface curvatures for clathrate formation and dissociation (or ice growth/melting) in narrow capillaries. The system is saturated with water (liquid volume greater than pore volume); therefore, the solid–vapor (or gas) and water–vapor interfaces are always outside the pores. Assuming cylindrical pores,  $r_2$  is infinite upon dissociation.

interface<sup>4</sup> (we refer to the ice–water equilibria here, because this transition can also occur in clathrate systems at low temperatures, and data for this system are presented in the companion paper to this work).<sup>11</sup> The higher phase pressure results in a higher fugacity and chemical potential of the components. This requires that clathrate dissociation occurs at a lower temperature for any given pressure, or at a higher pressure for any given temperature, when compared with bulk (unconfined) conditions. For ice–water equilibria, a similar situation applies, with the solid–liquid transition being depressed to lower temperatures at any given pressure and to lower pressures for any given temperature (the second case is the opposite to that for clathrate dissociation, because the ice–water phase boundary is depressed to lower temperatures at elevated pressures). For cylindrical pores (assumed here), the pressure of the solid phase (ice or hydrate),  $P_s$ , for a capillary of radius  $r$ , at any given temperature, is defined as<sup>4</sup>

$$P_s = P_l + \left( \frac{F\gamma_{sl} \cos \theta}{r} \right) \quad (1)$$

where  $P_l$  is the pressure of the liquid phase,  $F$  the shape factor of the solid–liquid interface,  $\gamma_{sl}$  the specific surface energy of the interface, and  $\theta$  the contact angle between the solid phase and the pore wall ( $0^\circ$ , if an unfrozen liquid layer is assumed).<sup>4</sup> The shape factor  $F$  is defined by the solid–liquid interfacial curvature,  $\kappa$ , in terms of the pore radius  $r$ , by

$$F = \kappa r \quad (2)$$

The solid–liquid interface curvature  $\kappa$  is defined as<sup>4,12,13</sup>

$$\kappa = \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3)$$

where  $r_1$  and  $r_2$  are the two orthogonal radii that describe the interface at any point. It is the difference between these two radii for solid-phase growth and for decomposition that defines the different interface curvatures  $\kappa$  for these transitions, as illustrated in Figure 1.

For a cylindrical pore, during solid-phase growth, if the solid–liquid interface is considered a hemispherical cap, then  $r_1$  and  $r_2$  are equal, giving a mean curvature of  $2/r$ . However, upon melting, although  $r_1$  remains constant,  $r_2$  is infinite (so  $1/r_2 \rightarrow 0$ , eq 3); thus, total curvature is  $1/r$ .<sup>12,13</sup> An infinite  $r_2$

value means that the solid–liquid interface does not retreat through a pore upon melting, but rather the solid cylinder should instantaneously melt along its entire length when stability conditions for the appropriate pore radius are surpassed.<sup>13</sup>

On the basis of the aforementioned information, we can use the Gibbs–Thomson equation to relate hydrate formation temperature depression (from bulk conditions) with pore size (the reader should refer to Clennell et al.<sup>4</sup> for a good summary of the derivation of equations presented here). According to this relationship, the temperature depression of clathrate growth (or water fusion to ice) in a cylindrical pore,  $\Delta T_{f,pore}$ , relative to the bulk (unconfined) formation temperature,  $T_{f,bulk}$ , is defined as

$$\frac{\Delta T_{f,pore}}{T_{f,bulk}} = -\kappa \left( \frac{\gamma_{sl} \cos \theta}{\rho_l \Delta H_{f,l}} \right) \quad (4)$$

where  $\rho_l$  is the liquid density and  $\Delta H_{f,l}$  is the specific enthalpy of the transition from liquid to solid (or from liquid + gas to solid hydrate). For growth,  $\kappa = 2/r$ , giving the relationship detailed in Clennell et al.:<sup>4</sup>

$$\frac{\Delta T_{f,pore}}{T_{f,bulk}} = -\left( \frac{2\gamma_{sl} \cos \theta}{\rho_l \Delta H_{f,l} r} \right) \quad (5)$$

Equation 5 has been employed to correlate clathrate dissociation data in the majority of studies to date.<sup>2,3,6–10</sup> However, as we have demonstrated, eq 5 actually describes the temperature depression of clathrate *growth* in cylindrical pores and is not applicable to experimental dissociation data. As proven by numerous studies, considerable hysteresis exists between the freezing point (on cooling) and melting point (on heating) of liquids in confined pores.<sup>14–16</sup> This is commonly attributed to the difference in solid–liquid interface curvatures,  $\kappa$ , during melting and freezing, which, as discussed, leads to a different shape factor  $F$  in each case.

For clathrate dissociation, or ice melting, eq 5 can be modified for an appropriate solid–liquid interface curvature of  $1/r$  to give

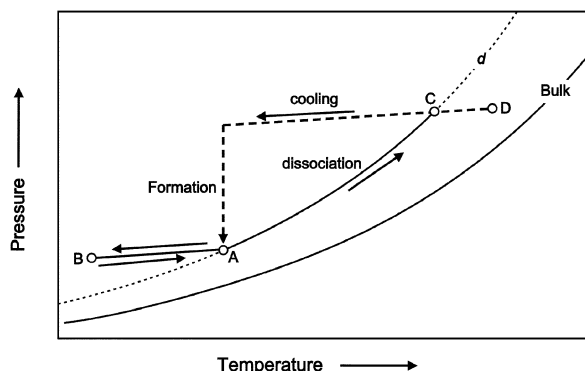
$$\frac{\Delta T_{m,pore}}{T_{m,bulk}} = -\left( \frac{\gamma_{sl} \cos \theta}{\rho_s \Delta H_{m,s} r} \right) \quad (6a)$$

or, in terms of pore diameter,

$$\frac{\Delta T_{m,pore}}{T_{m,bulk}} = -\left( \frac{2\gamma_{sl} \cos \theta}{\rho_s \Delta H_{m,s} d} \right) \quad (6b)$$

where  $\Delta T_{m,pore}$  is the difference between the pore ( $T_{m,pore}$ ) and bulk melting (dissociation) temperature,  $T_{m,bulk}$ , at any given pressure,  $\rho_s$  the solid density (the transition being reversed),  $\Delta H_{m,s}$  the latent heat of melting (equal to that of fusion),  $r$  the pore radius, and  $d$  the pore diameter (equal to  $2r$ ). This relationship has been successfully used to correlate both ice-melting and clathrate dissociation temperature depressions with pore diameter in the companion paper to this work.<sup>11</sup> The value for ice–water interfacial tension ( $32 \text{ mJ/m}^2$ ) derived from experimental data using the equation compares very closely with established literature values,<sup>17–20</sup> supporting the validity of the relationship.

It is important to note that eq 6 applies to a porous medium where the liquid volume is in excess of the pore volume, meaning that the only phase interface present within pores is the solid–liquid interface. For a saturated system at equilibrium, it is assumed that  $P_s > P_l = P_g$  ( $P_g$  is the gas or vapor pressure) and that chemical potentials are equal in all phases.  $P_g = P_l$ ,



**Figure 2.** Theoretical equilibrium dissociation path for a porous medium where all pores are of equal diameter  $d$ . During heating and consequent dissociation, the equilibrium pressure for the system will follow the univariant phase boundary for diameter  $d$ , as shown.

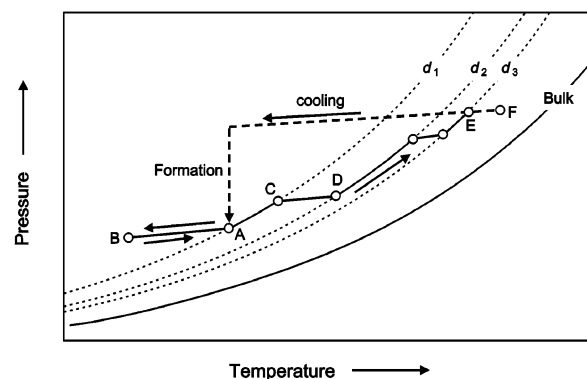
because the interface between the liquid and gas phases is external to the porous medium (gas does not intrude into the pores); thus, curvature is negligible. For an undersaturated system (pore volume greater than liquid volume), where gas intrudes into the pores, the added effect of potential high-curvature solid–gas and gas–liquid interfaces on phase pressures should also be considered.<sup>21</sup>

A further note, as pointed out by a reviewer, concerns the common requirement for supercooling (or subcooling) before crystallization can begin. This could be considered to be a potential explanation for the hysteresis between freezing and melting in porous media (no supercooling or superheating being required to initiate melting/dissociation). In laboratory experiments on bulk (unconfined) systems, supercooling well below the equilibrium transition temperature is generally required to initiate crystal growth within reasonable time scales. It would be expected that the same conditions apply to porous media, and this could potentially result in a marked difference between measured growth and decomposition temperatures. However, for systems where the solid phase is already present outside the pore network (under bulk conditions), no nucleation is required for growth in pores: only propagation of the solid formation front into the pore space is needed. In such systems, a marked hysteresis is still observed,<sup>15</sup> meaning that the difference between equilibrium melting and freezing temperatures cannot be attributed to supercooling alone—hence, the inference of interface curvature controls.

### Conceptual Model for Pore Clathrate Equilibria

The Gibbs–Thomson relationship presented here, in eq 6, requires that, for a single pore of diameter  $d$ , there will be a univariant phase boundary that defines the clathrate temperature and pressure stability field for this pore size. Thus, in accordance with the Gibbs phase rule, there is only one degree of freedom during equilibrium dissociation when pores are of equal diameter. On the basis of this observation, we can develop a simple conceptual model to predict the potential pattern of clathrate dissociation within a liquid-saturated porous medium (note that this model applies to constant volume systems, where pressure is not fixed).

**Dissociation in Pores of Equal Diameter.** Initially, we can consider a porous medium where all pores are of equal diameter  $d$ . The dissociation pattern for this system is demonstrated in Figure 2. The system is first cooled, and hydrate formation occurs (rapid, nonequilibrium growth under supercooled conditions is assumed here). If sufficient liquid is present, then the pressure will fall to the three-phase (pore-saturated) equilibrium

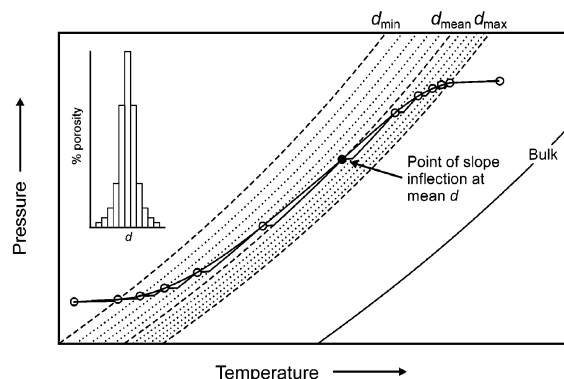


**Figure 3.** Theoretical equilibrium dissociation path for a porous medium with a simple pore size distribution. The sample has three different pore sizes, of radius  $d_1$ ,  $d_2$ , and  $d_3$ , which constitute 25%, 50%, and 25% of porosity, respectively, and where  $d_1 = 0.75d_2$  and  $d_3 = 1.25d_2$ . For simplicity, the pressure reduction associated with the volume of hydrate present in pores has been considered proportionate to the pore volume.

phase boundary for diameter  $d$  at point A. If it is assumed that all liquid (liquid available for clathrate formation, i.e., exclusive of any unfrozen film liquid on pore walls) was converted to hydrate to reach point A, then no further clathrate growth can occur and additional cooling will result in a linear pressure reduction associated with thermal contraction to point B. If the system is subsequently heated, then the first clathrate dissociation will occur when point A is surpassed, freeing liquid, and a three-phase equilibrium will again be achieved. All pores are of equal diameter; therefore, it follows that, upon further heating and progressive clathrate dissociation, the pressure of the system will rise with temperature, according to the phase boundary for diameter  $d$ . Conditions follow the boundary from point A to point C; thus, dissociation will result in progressively larger pore liquid-to-hydrate ratios until complete dissociation occurs at point C. The system then returns to initial conditions at point D.

**Dissociation across a Distribution of Pores Sizes.** On the basis of the aforementioned information, we can now introduce a simple distribution of pore sizes to the system. Consider a sample that has three different pore sizes of diameter  $d_1$ ,  $d_2$ , and  $d_3$ , constituting 25%, 50%, and 25% of porosity, respectively, where  $d_1 = 0.75d_2$  and  $d_3 = 1.25d_2$ . Clathrate stability in all pores will be defined by the appropriate univariant phase boundary for each diameter, as demonstrated in Figure 3. Because of the exponential effect of decreasing pore diameter on temperature depression, the  $\Delta T$  value between these boundaries increases as the value of  $d$  decreases.

Following the previous example for a single pore diameter, the system is first cooled to point A, where we make the assumption that all water (available water) is converted to clathrate. Further cooling to point B will thus again give no further hydrate formation. On heating past point A, the first drop of liquid will appear in pores of diameter  $d_1$  as dissociation in these pores commences. Conditions will then follow the phase boundary for  $d_1$  until complete clathrate dissociation for pores of this diameter at point C. Noting the assumption that all liquid in pores with diameters  $d_2$  and  $d_3$  is identified as clathrate, then further heating will not give dissociation until the first drop of liquid appears in pores of diameter  $d_2$  at point D, on the univariant boundary for this diameter. Conditions will then progress along the phase boundary for  $d_2$  until complete dissociation of clathrate in these pores, at which point dissociation halts until the phase boundary for  $d_3$  is reached. As for  $d_1$



**Figure 4.** Theoretical equilibrium dissociation path for a porous medium with multiple pore diameters (pore size distribution shown in inset). For simplicity, the pressure reduction associated with the volume of hydrate present in pores has been considered proportionate to the pore volume. During heating and consequent dissociation, the equilibrium pressure for the system will follow the univariant phase boundary for each pore radius in sequence.

and  $d_2$ , dissociation follows the phase boundary for  $d_3$  until complete clathrate decomposition at point E, following which the system returns to initial conditions at point F.

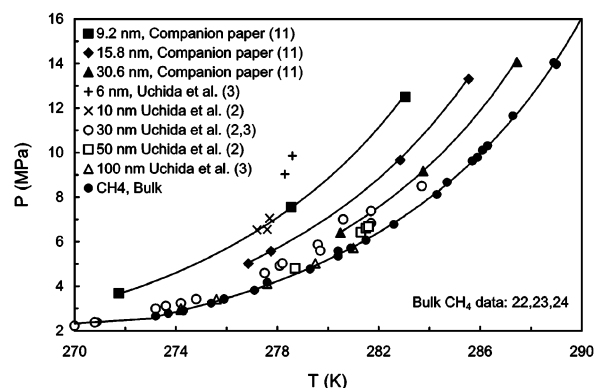
Introducing multiple pores of a Gaussian-like distribution, as shown in Figure 4, we see the development of a heating-curve pattern characteristic of those presented in both our work<sup>11</sup> and that of others.<sup>2,6–10</sup> For these heating curves, where the porous media have a continuous distribution (i.e., multiple, sequential diameters), each measured experimental equilibrium dissociation point should correspond to conditions on the univariant phase boundary for an appropriate pore diameter, as defined by the Gibbs–Thomson theory (eq 6) through the temperature depression ( $\Delta T_{m,pore}$ ) from bulk conditions ( $T_{m,bulk}$ ) at any given pressure.

### Influence of Test Procedures on Experimental Results

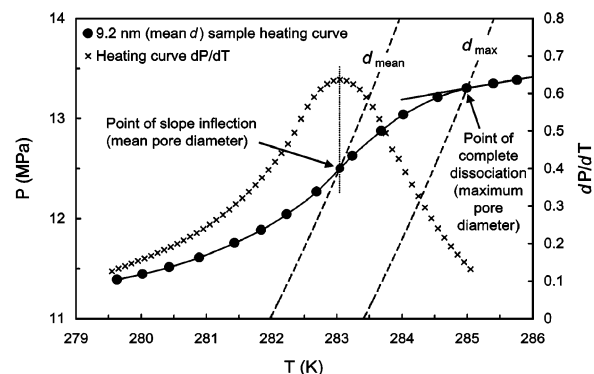
For isochoric (constant cell volume) clathrate equilibrium measurements, two experimental methods have been used to generate heating-curve data: (1) step heating,<sup>6–11</sup> and (2) continuous heating.<sup>2,3</sup> Continuous heating involves raising the system temperature at a constant rate to induce clathrate dissociation, whereas in step heating, the temperature is raised in steps, with sufficient time being given following each temperature step to allow the system to reach equilibrium (stable pressure). In the latter case, only equilibrium points are used in data interpretation and analysis.

Tohidi et al.<sup>25</sup> have demonstrated the superior accuracy and repeatability of hydrate equilibrium dissociation point data determined by the step-heating method, when compared to continuous heating. The principal problem with continuous heating is that equilibrium is practically unachievable in a system where temperature is constantly undergoing change, even if the rate of change is slow. Two common characteristics of disequilibrium resulting from continuous heating are dissociation at temperatures higher (or pressures lower) than the true equilibrium conditions and poor repeatability.<sup>25</sup>

Figure 5 shows equilibrium methane hydrate dissociation point data (mean pore diameter data) for mesoporous silica presented in the companion paper to this work (step-heating data), compared with the data of Uchida et al.<sup>2,3</sup> The significant scatter displayed by the latter, which suggests poor repeatability, could be explained by the use of continuous-heating methods to generate data.



**Figure 5.** Experimental equilibrium dissociation data (literature and from the companion paper) for methane clathrates in mesoporous silica and under bulk (unconfined) conditions.



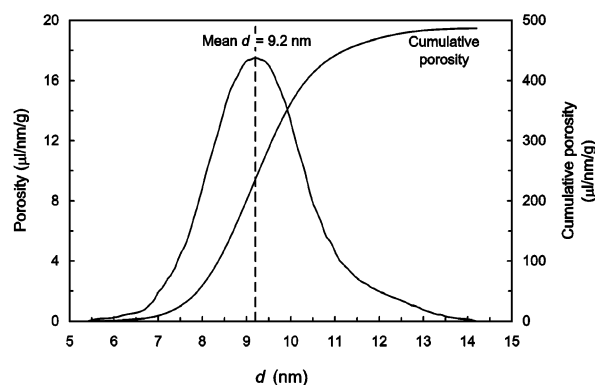
**Figure 6.** Experimental equilibrium step-heating curve for methane clathrates in porous silica glass (nominal pore diameter of 9.2 nm) (from the companion paper).<sup>11</sup> The inflection point of the heating curve (maximum of the  $dP/dT$  curve, plotted at 0.1 K intervals) approximates the dissociation in pores of the mean diameter of the distribution ( $d_{mean}$ ), as determined by NMR. This is confirmed from a comparison of data for dissociation in pores of  $d_{max}$  (complete pore dissociation) through the Gibbs–Thomson relationship.<sup>11</sup>

### Experimental Heating-Curve Interpretation

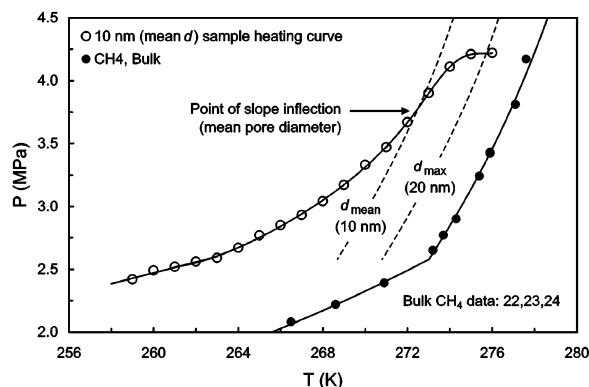
Accepting measured data from step-heating tests as equilibrium data, we can now discuss experimental results, with respect to the proposed conceptual model. Figure 6 shows a typical heating curve for clathrate dissociation in porous silica glass as observed in our work.<sup>11</sup> The dissociation pattern seen closely resembles that predicted by our model, essentially reflecting the cumulative porosity with pore diameter for the sample, as shown in Figure 7. This pattern was seen in the heating curves from all our experiments, for both methane and carbon dioxide clathrates.

It has previously been proposed (or assumed) that the mean (or nominal) pore radius cannot be used to interpret heating-curve data.<sup>6–10</sup> We have found this not to be the case. Assuming the volume of hydrate formed within pores is proportionate to the sample pore volume distribution, then, because the slope of the heating curve reflects the volume of hydrate dissociated with each temperature step, the point of slope inflection (from increasing to decreasing slope) should approximate the dissociation in pores with diameters close to the mean of the distribution (if the mean pore diameter matches the diameter of maximum porosity). This pattern is suggested by our model (Figure 4) and is observed in experimental heating curves from both our work and that of the literature (Figures 6 and 8). We therefore suggest that, contrary to previous proposals,<sup>6–10</sup> it is possible to interpret heating curves using the mean pore diameter as a reference.





**Figure 7.** Plot of pore diameter vs porosity and cumulative porosity for porous silica glass (mean pore diameter ( $d_{\text{mean}}$ ) of 9.2 nm (detectable  $d_{\text{max}} = 13.5$  nm)), as determined by NMR. Cumulative porosity is the sum of porosity for all pores of diameter  $d$  and smaller.



**Figure 8.** Methane clathrate heating-curve data from Smith et al.<sup>8</sup> for porous silica with a mean pore diameter of 10 nm. The inflection point of the heating curve and the point of complete dissociation correspond closely to the correlation predictions (see the companion paper)<sup>11</sup> for the mean and maximum pore diameters (diameters obtained from gas adsorption data presented by the authors).<sup>8</sup> Also shown is the bulk (unconfined) phase boundary for methane hydrates.

However, the aforementioned method of interpretation requires a relatively simple, unimodal pore size distribution, such as that of the porous silica samples used in our experimental work.<sup>11</sup> If the distribution is more complex, i.e., unevenly spread, with many peaks, then interpretation by this method may prove more difficult. A solution to this problem lies in the final dissociation point. Whatever the nature of the pore size distribution, the final dissociation point should always correspond to dissociation in pores of maximum diameter (of detectable porosity). Assuming that the maximum pore size is known with a reasonable degree of accuracy (i.e., from NMR or nitrogen absorption data), then this point can be used to correlate the pore diameter with temperature depression or to verify mean pore size data, as demonstrated in the companion paper to this work.<sup>11</sup>

The characteristic dissociation pattern we have described is clearly observed in heating-curve data presented by Uchida et al.<sup>2</sup> However, in both that study and recent work,<sup>3</sup> the authors determined the dissociation point for mean pore diameters using a method different from that proposed here. According to Uchida et al.,<sup>3</sup> dissociation conditions for mean pore diameters were determined as the intersection between the line of “maximum heating-curve inclination” and the “no dissociation” (thermal expansion) line (as shown in Uchida et al.<sup>2</sup>). On the basis of the effects of pore size distribution discussed here, this interpretation is likely to cause inaccuracy in results, generally underestimating inhibition, if the point taken is attributed to

mean pore diameter (or diameter of maximum porosity). This, in addition to possible errors resulting from continuous-heating methods as discussed previously, may further explain discrepancies between data presented by Uchida et al.<sup>2,3</sup> and those reported in our work (Figure 5).<sup>11</sup>

Contrary to our work<sup>11</sup> and that of Uchida et al.,<sup>2,3</sup> Wilder et al.,<sup>6</sup> Seshradi et al.,<sup>7</sup> Smith et al.,<sup>8,9</sup> and Zhang et al.<sup>10</sup> did not determine dissociation conditions for specific pore diameters (i.e., mean, maximum). Instead, they presented what we have called “heating-curve data” (these referenced authors used the term “hydrate equilibrium data”, because, correctly, each point represents equilibrium dissociation conditions for a particular pore diameter of a sample pore size distribution). These referenced authors proposed a *PTVr* model for dissociation in porous media, the theory behind which is similar to that for the model detailed here. However, contrary to our proposal, as noted, these workers concluded (or assumed) that the mean pore diameter could not be used to interpret heating-curve data.<sup>6–10</sup> This conclusion was based on the observation that different equilibrium pressures were possible for the same medium at any given temperature, and that different media could have similar equilibrium pressures at the same temperature. Wilder et al.<sup>6</sup> attributed this phenomenon to four factors: (1) the gas headspace-to-hydrate ratio after hydrate formation, (2) the temperature at which the first equilibrium measurement was made, (3) the volume of hydrate allowed to dissociate to establish equilibrium at this initial temperature, and (4) the pore volume distribution of the sample.

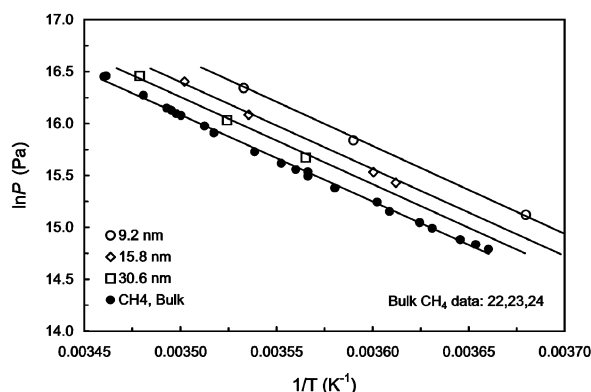
It is true that equilibrium pressures can vary with temperature for any given sample; however, this must not be confused with the equilibrium pressure for any given pore diameter. The temperature and pressure path of a heating curve for any given sample are dependent on numerous factors, including the initial pressure (i.e., the starting pressure, where generally the system is outside the hydrate stability zone and no hydrates are present), volumetric liquid-to-gas ratios, the volume of hydrate formed, the density of the hydrate phase (thus cage occupancy), and pore size distribution. However, the thermodynamic constraints discussed previously mean that the equilibrium dissociation pressure is fixed for a given pore diameter at a set temperature.

We speculate that the differing conclusions of Wilder et al.,<sup>6</sup> Seshradi et al.,<sup>7</sup> Smith et al.,<sup>8,9</sup> and Zhang et al.<sup>10</sup> may have arisen from the fact that heating curves measured by those authors could be considered incomplete when compared to those measured in our work. For many of the heating curves presented by those workers, the point of complete clathrate dissociation (or even slope inflection) is not shown, making interpretation, with respect to pore diameter, difficult.

When a complete heating curve is plotted, the final point of dissociation can be determined as the point where the slope becomes linear with increasing temperature (thermal expansion only), e.g., following  $d_{\text{max}}$  in Figures 6 and 8. For data reported by Smith et al.,<sup>8</sup> where the temperature range was sufficient to allow complete dissociation across the entire pore size distribution, the characteristic pattern suggested by our conceptual model can be observed (Figure 8), supporting our proposals.

### Enthalpy of Clathrate Dissociation

The specific enthalpy of clathrate dissociation,  $\Delta H_{\text{h,d}}$  ( $\Delta H_{\text{m,s}}$ ), is an important factor in eqs 5 and 6. Accurate values for  $\Delta H_{\text{h,d}}$  are required if experimental data are to be used to derive solid–liquid interfacial energies.<sup>3,11</sup> Experimental values for  $\Delta H_{\text{h,d}}$  have principally been determined through calorimetric investigations of clathrate equilibria under bulk conditions.<sup>26–28</sup> Several studies



**Figure 9.** Plot of reciprocal temperature vs the natural logarithm of pressure for experimental methane hydrate dissociation data (from the companion paper).<sup>11</sup> Linear relationships are fitted to bulk experimental data and univariant phase boundaries for appropriate experimental pore sizes (from the correlation presented in the companion paper to this work).<sup>11</sup> The comparable slopes mean  $\Delta H_{h,d}$  should be very similar for all.

suggest a potential dependence of latent heat on pore size for solid–liquid transitions, with apparently lower  $\Delta H_{m,s}$  values in mesopores, when compared to bulk conditions.<sup>1,15,16,29</sup> This phenomenon was noted by Handa and Stupin,<sup>1</sup> who presented differential scanning calorimetry (DSC) results that indicated a lower specific enthalpy of methane hydrate dissociation in mesoporous silica glass (45.9 kJ/mol, compared to 54.2 kJ/mol under bulk conditions). Similarly, Seshradi et al.,<sup>7</sup> applying the well-known Clausius–Clapeyron equation to the experimental hydrate equilibrium data, proposed a depression in the latent heat of propane clathrate dissociation in mesoporous silica. If the specific enthalpy of clathrate dissociation were a function of pore size, such a variation would have significant implications for the modeling of clathrate systems in porous media.

Many workers have assessed the suitability of the Clausius–Clapeyron equation for the calculation of  $\Delta H_{h,d}$  from three-phase equilibrium data.<sup>30,31</sup> According to this relationship, the slope of reciprocal temperature,  $1/T$ , versus the natural logarithm of pressure,  $\ln P$ , can be related to  $\Delta H_{h,d}$  by

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = -\left(\frac{\Delta H_{h,d}}{zR}\right) \quad (7)$$

where  $R$  is the universal gas constant and  $z$  is the gas compressibility factor. However, discrepancies exist among  $\Delta H_{h,d}$  values derived in this manner,<sup>30,31</sup> with the results being generally higher than those measured experimentally.<sup>26–28</sup> It must be remembered that the Clausius–Clapeyron equation was originally intended for liquid–vapor equilibria and requires a considerable number of assumptions to be made for its adaptation to clathrate systems.<sup>30,31</sup>

In the model of Seshradi et al.,<sup>7</sup> authors employed eq 7 to derive  $\Delta H_{h,d}$  for clathrate dissociation from heating-curve data (pressures were converted to fugacities). However, even if the Clausius–Clapeyron equation is accepted as being valid for this type of phase transition, it is not applicable to clathrate heating curves, because these data do not represent a univariant phase boundary for a single pore radius—a requirement of eq 7.<sup>30,31</sup> In Figure 9, it can be seen that the slopes of  $\ln P$  against reciprocal temperature ( $1/T$ ) for univariant phase boundaries fitted to our data (from the correlation presented in the companion paper)<sup>11</sup> closely parallel that of the bulk boundary; thus, eq 7 should yield similar  $\Delta H_{h,d}$  values for all pore sizes.

The apparent reduction in  $\Delta H$  measured by DSC can actually be attributed to the presence of an unfrozen layer of liquid between the solid phase and the pore wall.<sup>15</sup> In DSC,  $\Delta H$  is estimated from the integrated area of the endothermic peak for the appropriate mass of confined liquid.<sup>1,15,29</sup> The presence of an unfrozen liquid layer may therefore result in a lower calculated latent heat for pore solid–liquid transitions. We thus conclude that the apparent relationship between  $\Delta H_{h,d}$  reduction and pore size suggested by Seshradi et al.<sup>7</sup> merely reflects the more-gentle slope of heating curves when compared to equilibrium phase boundaries (of both pore and bulk hydrates).

In the companion paper to this work,<sup>11</sup> we found that using bulk values for  $\Delta H_{h,d}$  gave good results that are internally consistent. Employing the bulk value for the specific enthalpy of fusion of ice ( $\Delta H_{f,i}$ ), we obtained values for ice–water interfacial tension from all pore size dissociation data which are consistent with established literature values (as previously noted). We therefore conclude that  $\Delta H_{h,d}$  is conservative and not a strong function of pore (or crystal) size. This may be expected where pore sizes are in excess of crystal unit cell size, i.e., where the pore solid retains the structure of the bulk phase.

## Conclusions

The aim of this paper was to clarify clathrate dissociation behavior in porous materials, with respect to pore size distribution, and to resolve contradictions concerning the measurement and interpretation of experimental data for such systems. From this review, we can draw the following conclusions:

(1) Step heating provides a more-reliable method for isochoric determination of clathrate dissociation conditions in porous media, when compared to continuous-heating techniques.

(2) In porous media with a pore size distribution, clathrates will dissociate over a range of equilibrium temperatures and pressures along a pressure–temperature–volume–pore radius (PTVr) path reflecting this distribution.

(3) The equilibrium dissociation pressure for a particular pore size at any given temperature should correspond to the univariant phase boundary for that pore size (i.e., for any single pore diameter, the system has only one degree of freedom).

(4) For samples with a simple, unimodal distribution, it is possible to determine dissociation conditions for the mean pore size from the slope of the heating curve, if the mean corresponds to pores of dominant porosity. For all porous materials, the final dissociation point can be attributed to dissociation on the univariant phase boundary for pores of maximum diameter (of detectable porosity). These data, through the Gibbs–Thomson relationship, may be used to verify the reliability of mean pore size dissociation point data (where a suitable dissociation temperature depression is observed).

(5) When modeling clathrate dissociation (or ice melting) in porous media, the Gibbs–Thomson relationship should be modified according to the established hysteresis conditions. We have assumed shape factors of 2 (formation) and 1 (decomposition) for clathrates (and ice) in cylindrical pores, although other shape factors could be used if there is more information on pore morphology.

(6) In the absence of reliable evidence to the contrary, the enthalpy of clathrate dissociation in pores can be assumed to be equal to the bulk value.

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