

Supporting Information for: Kinetics of sII, and Mixed sI/sII, Gas-hydrate Growth for a Methane/Propane Mixture Using Neutron Diffraction

A. Klapproth¹, R.O. Piltz^{1}, S.J. Kennedy^{1,2}, and K.A. Kozielski³*

¹ Australian Centre for Neutron Scattering, Lucas Heights, Australia

² European Spallation Source, Lund, Sweden

³ CSIRO Energy, Clayton North, Australia

Pressure Cell

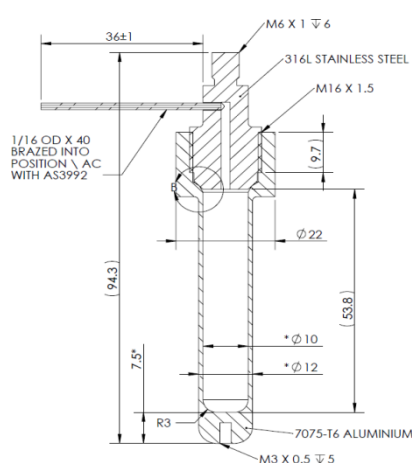


Figure 1. Dimensions and materials of the aluminum pressure cell.

Wombat Experimental Configuration

Wombat was operated at a wavelength of $\sim 2.4 \text{ \AA}$ with vertical focusing to increase the beam intensity, and using the oscillating tertiary collimator. Diffraction data was collected as 2D images from the continuous detector bank of 120° . The raw data was reduced to conventional 1D powder patterns using the *LAMP* software[1]. Strong powder lines were obtained from the aluminium of the pressure cell, though they were well separated from the low angle powder lines of the ice and hydrate phases. Powder diffraction patterns were collected at intervals of 1 minute for a period of 4 to 15 hours.

* E-mail: ross.piltz@ansto.gov.au

Quantitative Phase Analysis

Three Bragg peaks were used for the Quantitative Phase Analysis (QPA): (hkl) = (321) of the sI phase; (531) of sII; (110) of ice. The respective scattering angles for these peaks were approximately $2\theta = 45.3^\circ$, 49.7° , and 65.3° . The program *LAMP* was used to fit the peaks using a Gaussian peak shape and a linear local background. The three peaks were chosen for being relatively strong and having easily correctable overlap, if any, with peaks from the other phases. The second peak, (531) of sII, is closely overlapped with the smaller (410) of the sI phase. The third peak, (110) of ice, is partially overlapped by a pair of weak peaks, the (432) & (520) of the sI phase and the (731) & (553) of the sII phase. For each experiment, the integrated peak intensities were scaled by the initial value of the (110) ice peak. The phase fractions $f(sI)$, $f(sII)$, and $f(ice)$ were obtained using linear algebra and the peak intensities calculated using *PowderCell 2.4[2]*.

Normally, QPA uses phase fractions that are proportional to the mass of the phase. In our case it is more convenient to use phase fractions that are proportional to the number of D₂O molecules in the phase. The conservation of D₂O molecules is then easily expressed by $f(\text{total}) = 1$, where the total phase fraction is $f(\text{total}) = f(sI) + f(sII) + f(ice) + f(\text{water})$. To obtain this type of phase fraction, the peak intensities calculated using *PowderCell* are multiplied by the volume per D₂O molecule for that phase.

As part of an accuracy check, the relatively weak but non-overlapped (440) peak of sII was also fitted. The $f(sII)$ values obtained using this peak were found to be in agreement with those obtained from the overlapped peaks, thus confirming the validity of our approach. It also confirms that the peak intensities of the hydrate phases were not significantly affected by preferred orientation.

The (002) peak of the ice phase at $2\theta \sim 39^\circ$ was also measured as a check for the presence of preferred orientation in the ice phase. Ice was often formed from liquid water due to hydrate decomposition near the end of an experiment. In this case severe preferred orientation was common. For the finely ground ice at the start of an experiment, no preferred orientation was observed prior to the pressurization of the sample cell.

Sample Attenuation Factor

All atoms in the sample, C, O, H, and D have negligible neutron absorption, though an effective attenuation of the neutron beam occurs due to their large incoherent scattering cross-section of the H atoms. The value for this cross-section varies from the *bound atom* value of 80 to the *free atom* value of 20 barns. A commonly used approximation[3] estimates

an incoherent cross-section of 67 barns. This approximation was based on a transition metal complex, and it is expected that the less bound gaseous and caged methane/propane molecules in hydrate will behave closer to the free atom limit and thus have a value significantly less than 67 barns.

The attenuation correction factor depends on the amount of hydrogen in the sample, which can be calculated from the methane gas pressure and the phase fractions of the hydrate sI and sII phases. An iterative method is used that estimates the phase fraction, calculates the attenuation factor and then recalculates a new phase fraction. The method is repeated until convergence. Tabulated absorption correction for a cylindrical sample [4] were approximated in the 2θ range of 45 to 65° by $A^* = 1 + 1.58 (\mu R) + 1.78 (\mu R)^2$, where μ is the linear absorption coefficient and R is the cylinder radius.

The packing ratio of the ground ice sample was measured as 0.58. It has been assumed that all cages of sI and the small cages of sII are occupied by a single methane molecule, and that the large cages of sII are occupied by a propane molecule. Due to depletion, the mole fraction of propane in the free gas of the cell is expected to vary from 10% to 0%. For the calculation of μ , a mole fraction of 5% propane, a temperature of 0° C, and the ideal gas law is assumed. For an incoherent cross-section of 67 barns for the hydrogen atoms, calculated value of μR is

$$\mu R = 0.0016 P + 0.36 f(sI) + 0.48 f(sII) \quad (S1)$$

where P is the pressure in bar and $f()$ are the phase fractions for sI and sII. It was found by trial and error that the constants in this equation must be reduced by 40 to 50%, the final result being $\mu R = 0.00096 P + 0.18 f(sI) + 0.24 f(sII)$. Such values are consistent with an incoherent cross-section of ~40 barns for each hydrogen atom, and slightly less than complete filling of the cages.

Water Diffuse Scattering

The background intensity of our diffraction patterns show significant contributions from the incoherent scatter mentioned above, and the diffuse scatter from liquid water. The water diffuse scatter can be identified as a broad increase in the background centred at a d-spacing of ~3 Å, which corresponds in our case to an angle of $2\theta \approx 50^\circ$. The background from the incoherent scatter is much more uniform, showing a much slower 2θ dependence due to the Placzek correction[5]. This allows the water diffuse and the incoherent components of the background to be extracted by comparing the background at two angles, in our case we use the results from the fit of the 50° and 65° Bragg peaks. The water diffuse component is

proportional to the amount of liquid water in the sample, while the incoherent component is proportional to the effective attenuation parameter μ . We can therefore write

$$f(\text{water}) = S_{\text{water}}(I_B(50^\circ) - a_1 I_B(65^\circ)) \quad (\text{S2a})$$

$$\mu R = S_{\text{incoh}}(I_B(65^\circ) - a_2 I_B(50^\circ)) \quad (\text{S2b})$$

where I_B is the background intensity with the time independent value subtracted, and S_{water} and S_{incoh} are unknown scale factors. The parameters a_1 , a_2 , and S_{incoh} are readily determined by trial and error since $f(\text{water})$ is zero until ice melting occurs, and the size of μR is well determined by eq S1. The values for a_1 vary from 1.24 to 1.33, a_2 has a constant value of 0.25, and S_{incoh} varies from 0.30 to 0.48. The variation in the latter is apparently a result of differences in experimental conditions between data sets, e.g. focussing of the monochromators, difference in neutron shielding of the sample holder and detector.

The initial values of S_{water} were estimated for each sample using plots of the total phase fraction, $f(\text{total}) = f(s\text{I}) + f(s\text{II}) + f(\text{ice}) + f(\text{water})$. An example is shown in Figure S1 where both $S_{\text{water}} = 0.4$ and 1.8 appear unreasonable, the former due to the low final $f(\text{total})$ of ~ 0.2 , the latter due to the rapid rise in $f(\text{total})$ at 320 minutes. Alternatively, the plots for $S_{\text{water}} = 0.7$ and 1.1 appear equally believable, which results in the estimate $S_{\text{water}} = 0.9 \pm 0.2$. Independent of the value chosen, all plots in Figure S1 show a significant drop of 20 to 40% at 150 minutes, which accompanies the melting of ice (see Figure 2). This effect was seen in all samples and its degree depends on the fraction of ice at the onset of melting. It is believed that a proportion of the liquid water drains to the lower part of the sample cell where it is not illuminated by the neutron beam. This possibility was tested by raised the sample cell relative to the neutron beam which resulted in an almost doubling of the water component relative to that of hydrate. The same effect occurs on the decomposition of hydrate to water, the final $f(\text{total})$ dropping to values of 0.5 to 0.7. This amount is consistent with a simple calculation based on the packing density of the ice and the geometry of the sample cell and neutron beam. From the initial estimates of S_{water} it was found to be approximately six times larger than S_{incoh} , which allowed us to use the simple relationship of $S_{\text{water}} = 6 \times S_{\text{incoh}}$.

It is admitted that this calculation of the water component will not be very accurate. The process is multi-step, and contains several assumptions. Despite this, we believe the calculated water phase fractions are useful as indicators of the amount of liquid water present, even if their accuracy is questionable.

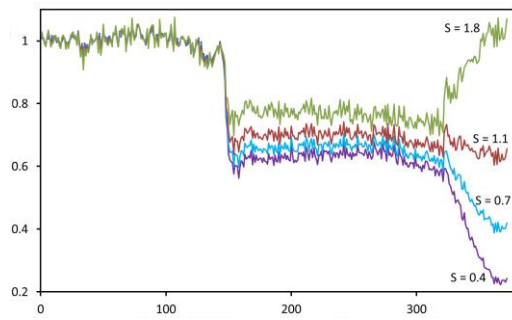


Figure S1: Total phase fraction versus experiment time in minutes for Sample 3b as calculated from different S_{water} values. Plots are marked with the S_{water} value used.

Final Calculated Phase Fractions

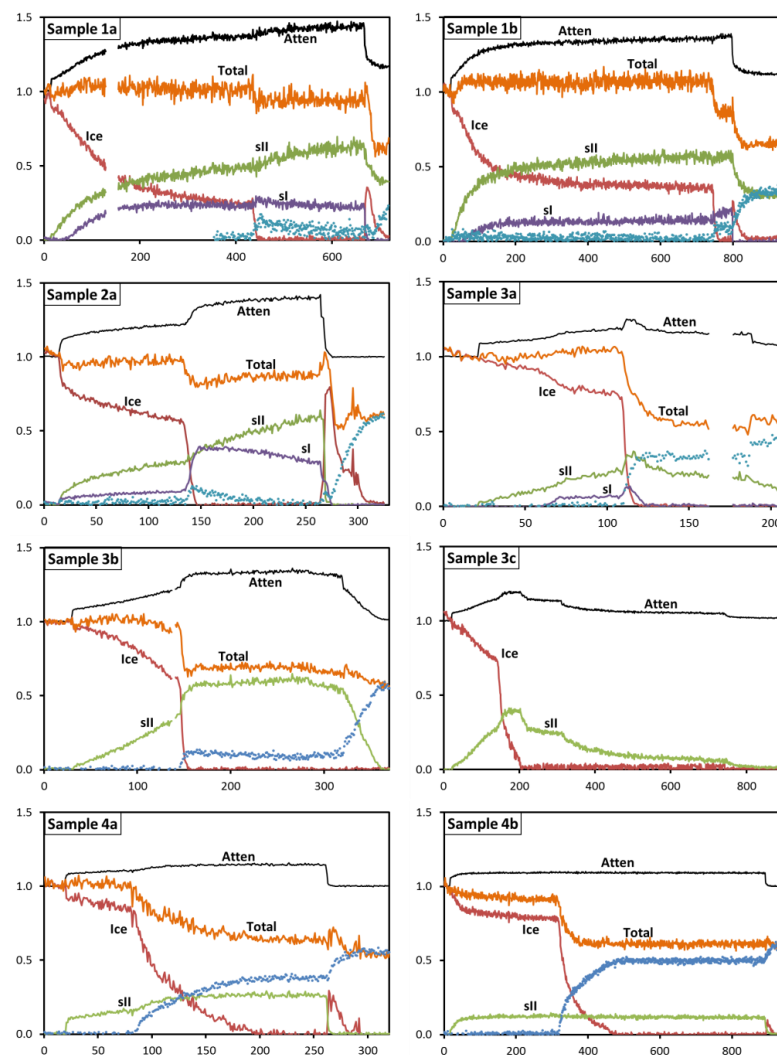


Figure S2: Phase fractions of sI, sII, and Ice phases versus time in minutes for all eight samples. Solid circles are estimates of the phase fraction for liquid D_2O water, the line marked as Total is the sum of all phase fractions, while the line marked as Atten is the sample attenuation factor.

Estimate of $f(\text{sII})$ growth used in: Hydrate Growth during Ice Melting

First, we make some rough estimates about the water layer geometry. Assuming the hydrate surface has the same surface area as the initial ice particles, and that these particles are 30 μm spheres, then the surface area is estimated to be 0.3 m^2 . From Figure 2 we note that 10% of the total D_2O in the cell appears as liquid during ice melting, and when combined with a surface area of 0.3 m^2 , this gives a water layer thickness of 0.5 μm .

Diffusion constant for propane in water at 273K[6]: $D = 7.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

Propane molar fraction in water[7] for 0.32% propane in methane at 50 bar, 273K: 9×10^{-6}

→ Propane molar concentration, $C = 0.5 \text{ mol m}^{-3}$

Assume propane molar concentration gradient across water layer is $C / (0.5 \mu\text{m})$

→ Propane molar flux, $J = D C / (0.5 \mu\text{m}) = 7.5 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$

→ Propane molar flow = $J \times (0.3 \text{ m}^2) = 2 \times 10^{-4} \text{ mol s}^{-1}$

Equation referenced in: Heterogeneous Occupancy Models

$$y_{\text{C}_3} = 0.1 + (Z T / 273.2(\text{K}) / P)$$

$$\left\{ \begin{aligned} &0.943(\text{bar} \cdot \text{mmol}^{-1}) n_{\text{H}}^{120}(\text{CH}_4) - 8.491(\text{bar} \cdot \text{mmol}^{-1}) n_{\text{H}}^{120}(\text{C}_3\text{H}_8) \\ &+ (3.68(\text{bar}) \theta_{\text{C}_1}(\text{sI}, \text{S}) + 11.03(\text{bar}) \theta_{\text{C}_1}(\text{sI}, \text{L})) (f(\text{sI}) - f^{120}(\text{sI})) \\ &- (44.75(\text{bar}) \theta_{\text{C}_3}(\text{sII}, \text{L}) - 9.94(\text{bar}) \theta_{\text{C}_1}(\text{sII}, \text{S}) - 4.97(\text{bar}) \theta_{\text{C}_1}(\text{sII}, \text{L})) \\ &\quad (f(\text{sII}) - f^{120}(\text{sII})) \end{aligned} \right\} \quad (\text{S3})$$

where $f^{120}()$ and $n_{\text{H}}^{120}()$ are the values of $f()$ and $n_{\text{H}}()$ at 120 minutes, the latter being calculated using eq 2.

Equation derivation for: Estimating Depletion of Gaseous Propane

The sample cell has a total volume of 4.0 ml and is filled with 2.8 ml of powdered D_2O ice. From the measured packing ratio of the ice, 0.58, the volume of the solid ice is therefore 1.62 ml. The total void in the sample cell is 1.2 ml above the ice powder plus 1.18 ml between the powdered ice grains. For an ideal gas at 1 bar and 273.2K, 1 mmol occupies a volume of 22.40 ml, so the amount of gas in the sample cell void is $2.38/22.40 = 0.106 \text{ mmol}$ under these conditions. Generalizing this value to a real gas at arbitrary temperatures and pressures results in $0.106(\text{mmol} \cdot \text{bar}^{-1}) P / (Z T / 273.2(\text{K}))$. The amounts of gaseous methane and propane in the gas mixture of the void space are

$$n_G(\text{CH}_4) = 0.106(\text{mmol} \cdot \text{bar}^{-1}) \left(\frac{P(1-y_{C3})}{Z T/273.2(\text{K})} \right) \quad (\text{S4a})$$

$$n_G(\text{C}_3\text{H}_8) = 0.106(\text{mmol} \cdot \text{bar}^{-1}) \left(\frac{P y_{C3}}{Z T/273.2(\text{K})} \right) \quad (\text{S4b})$$

where y_{C3} is the unknown mole fraction of gaseous propane in the void space.

The amount of methane and propane molecules contained within the hydrate are calculated from the sI and sII phase fractions and the initial 89.6 mmol of D₂O ice, the latter calculated from 1.62 ml of ice at 0° C using a density of 1.106 g/ml. The sI hydrate has 2 small and 6 large cages for a framework of 46 water molecules, while the sII hydrate has 16 small and 8 large cages for a framework of 136 water molecules. As the hydrate phase fractions have been scaled versus the number of water molecules in their frameworks, the amount of gaseous molecules stored in each hydrate cage is given by $89.6(\text{mmol}) N_{\text{Cages}}/N_{\text{Water}} \theta f$. N_{Cages} and N_{Water} are the number of cages and water molecules (as given above) while θ and f are the cage occupancy and phase fraction for the hydrate in question. The amounts of methane and propane gas within the hydrates are obtained by summing these terms,

$$\begin{aligned} n_H(\text{CH}_4) = & \left(3.90(\text{mmol}) \theta_{C1}(\text{sI}, \text{S}) + 11.69(\text{mmol}) \theta_{C1}(\text{sI}, \text{L}) \right) f(\text{sI}) \\ & + \left(10.54(\text{mmol}) \theta_{C1}(\text{sII}, \text{S}) + 5.27(\text{mmol}) \theta_{C1}(\text{sII}, \text{L}) \right) f(\text{sII}) \end{aligned} \quad (\text{S5a})$$

$$n_H(\text{C}_3\text{H}_8) = 5.27(\text{mmol}) \theta_{C3}(\text{sII}, \text{L}) f(\text{sII}) \quad (\text{S5b})$$

where $\theta_X(Y, Z)$ denotes the methane or propane occupancies ($X=C1$ or $C3$) of the small or large cages ($Z=S$ or L) of the hydrate phase ($Y=sI$ or sII).

The sample cell is maintained at constant pressure by the inflow of feed gas (10% propane in methane) from the gas supply rig. The sample cell and supply rig are connected by long thin tubing which restricts gas diffusion to negligible amounts, thereby preventing equilibration of gas concentrations between the sample cell and the supply rig. As a result, the gas molecules within the sample cell are present at a ratio of 9:1 methane to propane. This leads to the mass balance condition that the total of gaseous and hydrate methane (sum of eqs S4a and S5a) must be 9 times the total of gaseous and hydrate propane (sum of eqs S4b and S5b).

$$n_G(\text{CH}_4) + n_H(\text{CH}_4) = 9 n_G(\text{C}_3\text{H}_8) + 9 n_H(\text{C}_3\text{H}_8) \quad (\text{S6})$$

By substituting eqs S4 and S5 into eq S6 the resultant equation can be solved for the variable y_{C3} resulting in eq 3 of the manuscript. This is explicitly shown below. For clarity sake, the units of the numeric values are not shown.

Using eqs(S4,S5) we expand the LHS and RHS of eq S6 as:

$$\begin{aligned}
 n_G(\text{CH}_4) + n_H(\text{CH}_4) &= 0.106 P / (Z T / 273.2) (1 - y_{C3}) \\
 &+ (3.90 \theta_{C1}(sl,S) + 11.69 \theta_{C1}(sl,L)) f(sl) \\
 &+ (10.54 \theta_{C1}(sll,S) + 5.27 \theta_{C1}(sll,L)) f(sll) \\
 9 * n_G(\text{C}_3\text{H}_8) + 9 * n_H(\text{C}_3\text{H}_8) &= 9 * 0.106 P / (Z T / 273.2) y_{C3} \\
 &+ 9 * 5.27 \theta_{C3}(sll,L) f(sll) \\
 &= 0.954 P / (Z T / 273.2) y_{C3} + 47.43 \theta_{C3}(sll,L) f(sll)
 \end{aligned}$$

Equating the above LHS and RHS terms:

$$\begin{aligned}
 &0.106 P / (Z T / 273.2) (1 - y_{C3}) \\
 &+ (3.90 \theta_{C1}(sl,S) + 11.69 \theta_{C1}(sl,L)) f(sl) \\
 &+ (10.54 \theta_{C1}(sll,S) + 5.27 \theta_{C1}(sll,L)) f(sll) \\
 &= 0.954 P / (Z T / 273.2) y_{C3} + 47.43 \theta_{C3}(sll,L) f(sll)
 \end{aligned}$$

Which can be rearranged to:

$$\begin{aligned}
 &0.106 P / (Z T / 273.2) \\
 &+ (3.90 \theta_{C1}(sl,S) + 11.69 \theta_{C1}(sl,L)) f(sl) \\
 &+ (10.54 \theta_{C1}(sll,S) + 5.27 \theta_{C1}(sll,L)) f(sll) - 47.43 \theta_{C3}(sll,L) f(sll) \\
 &= 0.954 P / (Z T / 273.2) y_{C3} + 0.106 P / (Z T / 273.2) y_{C3}
 \end{aligned}$$

And further to:

$$\begin{aligned}
 &1.060 P / (Z T / 273.2) y_{C3} = \\
 &0.106 P / (Z T / 273.2) \\
 &+ (3.90 \theta_{C1}(sl,S) + 11.69 \theta_{C1}(sl,L)) f(sl) \\
 &+ (10.54 \theta_{C1}(sll,S) + 5.27 \theta_{C1}(sll,L) - 47.43 \theta_{C3}(sll,L)) f(sll)
 \end{aligned}$$

And further to:

$$\begin{aligned}
 y_{C3} &= 0.106 P / (Z T / 273.2) / (1.060 P / (Z T / 273.2)) \\
 &+ \{ \\
 &\quad (3.90 \theta_{C1}(sl,S) + 11.69 \theta_{C1}(sl,L)) f(sl) \\
 &\quad + (10.54 \theta_{C1}(sll,S) + 5.27 \theta_{C1}(sll,L) - 47.43 \theta_{C3}(sll,L)) f(sll) \\
 &\quad \} / (1.060 P / (Z T / 273.2)) \\
 &= 0.1 + \{ (3.68 \theta_{C1}(sl,S) + 11.03 \theta_{C1}(sl,L)) f(sl) \\
 &\quad + (9.94 \theta_{C1}(sll,S) + 4.97 \theta_{C1}(sll,L) - 44.75 \theta_{C3}(sll,L)) f(sll) \} / (P / (Z T / 273.2)) \\
 &= 0.1 + (Z T / 273.2 / P) \{ (3.68 \theta_{C1}(sl,S) + 11.03 \theta_{C1}(sl,L)) f(sl) \\
 &\quad - (44.75 \theta_{C3}(sll,L) - 9.94 \theta_{C1}(sll,S) - 4.97 \theta_{C1}(sll,L)) f(sll) \}
 \end{aligned}$$

The final representation being eq 3 of the manuscript.

REFERENCES

1. LAMP, the Large Array Manipulation Program.
http://www.ill.fr/data_treat/lamp/lamp.html.
2. Kraus, W. and G. Nolze, *PowderCell for Windows-Version 2.4-Structure Visualisation/Manipulation, Powder Pattern Calculation and Profile Fitting*. Federal Institute for Materials Research and Testing, Berlin, Germany, 2000.
3. Howard, J., et al., *Determination of the neutron absorption cross section for hydrogen as a function of wavelength with a pulsed neutron source*. Journal of Applied Crystallography, 1987. **20**(2): p. 120-122.
4. Hamilton, W., *International Tables for X-ray Crystallography, vol. IV*. Birmingham: Kynoch Press.(Present distributor Kluwer Academic Publishers, Dordrecht.), 1974: p. 273-284.
5. Placzek, G., *The scattering of neutrons by systems of heavy nuclei*. Physical review, 1952. **86**(3): p. 377.
6. Witherspoon, P. and D. Saraf, *Diffusion of methane, ethane, propane, and n-butane in water from 25 to 43*. The Journal of Physical Chemistry, 1965. **69**(11): p. 3752-3755.
7. Sloan, E. and C. Koh, *CSMGem a phase-equilibrium calculation program package accompanying the following book, in Clathrate Hydrates of Natural Gases*. 2007, CRC Press Florida.