

Development of a high pressure automated lag time apparatus for experimental studies and statistical analyses of nucleation and growth of gas hydrates

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(Received 7 April 2011; accepted 1 June 2011; published online 24 June 2011)

Nucleation in a supercooled or a supersaturated medium is a stochastic event, and hence statistical analyses are required for the understanding and prediction of such events. The development of reliable statistical methods for quantifying nucleation probability is highly desirable for applications where control of nucleation is required. The nucleation of gas hydrates in supercooled conditions is one such application. We describe the design and development of a high pressure automated lag time apparatus (HP-ALTA) for the statistical study of gas hydrate nucleation and growth at elevated gas pressures. The apparatus allows a small volume ($\approx 150 \mu\text{l}$) of water to be cooled at a controlled rate in a pressurized gas atmosphere, and the temperature of gas hydrate nucleation, T_f , to be detected. The instrument then raises the sample temperature under controlled conditions to facilitate dissociation of the gas hydrate before repeating the cooling-nucleation cycle again. This process of forming and dissociating gas hydrates can be automatically repeated for a statistically significant (> 100) number of nucleation events. The HP-ALTA can be operated in two modes, one for the detection of hydrate in the bulk of the sample, under a stirring action, and the other for the detection of the formation of hydrate films across the water-gas interface of a quiescent sample. The technique can be applied to the study of several parameters, such as gas pressure, cooling rate and gas composition, on the gas hydrate nucleation probability distribution for supercooled water samples. © 2011 American Institute of Physics. [doi:10.1063/1.3602926]

I. INTRODUCTION

Clathrate hydrates have been the subject of intense scientific and industrial research for some time since they have been suggested as gas storage media, and as a potential energy source. Other important applications have been reviewed by several authors.^{1–9}

Formation of gas hydrates can also be problematic. For example, in transportation of natural gases, gas hydrates can block pipelines where pressures are high and temperatures are low, and prevent the flow of production fluids and/or cause damage to the pipes.⁹

In oil and gas production, strategies for hydrate prevention and mitigation have been developed.⁹ These include the addition of chemicals which act as thermodynamic or kinetic hydrate inhibitors (THI/KHI), direct heating or depressurization.^{9,10} However, as gas reserves decline, more remote and deeper gas fields are being exploited, which require more effective inhibition strategies. At the same time, better understanding of mechanisms of hydrate nucleation and growth, and quantification of hydrate formation and agglomeration risks, can help engineers to operate their facilities more economically in these environments.

Conventional methods of studying nucleation and growth of gas hydrates involve recording of the “induction time” prior to the nucleation of a sample at a constant temperature below the equilibrium hydrate dissociation temperature, T_{eq} , of a sample.^{9,11–13} However, the stochastic nature of the nucleation process means that induction time is often irreproducible, and can vary significantly from sample to sample, especially at conditions close to T_{eq} , where the driving force for hydrate formation is low.^{9,11,13} Analysis of nucleation probability in such systems necessitates the collection of statistically significant data sets which can be experimentally challenging, given the time consuming nature of the measurements, and the requirement for fine control of gas pressure and temperature.

We have developed a new instrument which allows the acquisition of large sample sets of gas hydrate nucleation and growth data with a view to investigating the mechanisms underlying the formation kinetics of gas hydrates,¹⁴ the high pressure automated lag time apparatus (HP-ALTA) based on earlier work by Haymet, Heneghan, and Wilson.^{15–17}

The technique exploits the increased probability of nucleation in a supercooling liquid as the temperature is decreased below the thermodynamic phase boundary for hydrate formation in a region of the pressure-temperature (P - T) phase diagram. In essence, the sample is subjected to an increased driving force for hydrate formation through the application of

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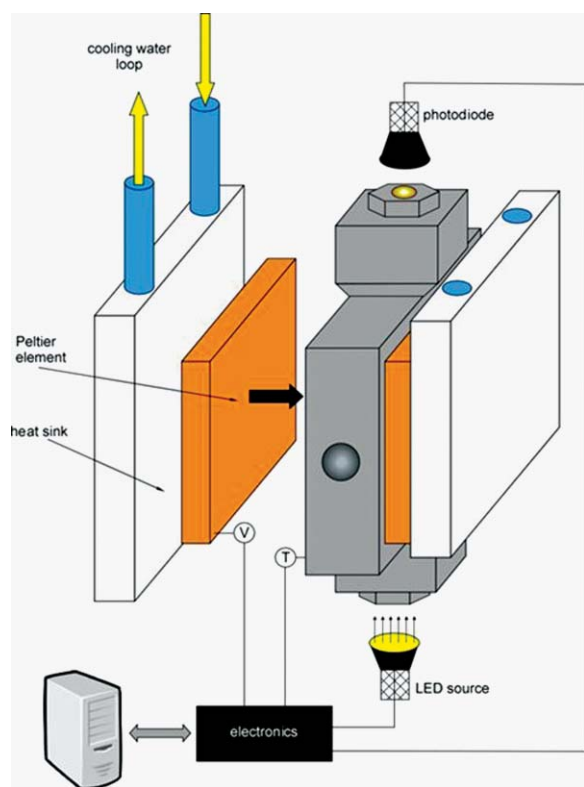


FIG. 1. (Color online) Schematic illustration of high pressure automated lag time apparatus (HP-ALTA).

a cooling ramp. The imposition of an increasing driving force effectively compresses a large variation in the induction time at a constant driving force to a much narrower variation in the lag time under a cooling ramp.

In this paper, we describe the design and the operation of the instrument. Only a small volume of sample ($\approx 130 \mu\text{l}$) is required for collection of a statistically significant number of nucleation events under identical conditions.

II. DESCRIPTION OF THE INSTRUMENT

The automated lag time apparatus (ALTA) was originally designed for the statistical study of ice nucleation in a glass tube under atmospheric pressure.^{15,16} Here we designed and built an HP-ALTA to achieve the same statistically valid data sets for the formation of gas hydrates at elevated gas pressure.

The HP-ALTA pressure chamber is made of stainless steel ($\sim 5 \text{ cm} \times 5 \text{ cm} \times 2 \text{ cm}$), the pressurized volume of the cell is comprised of two 6 mm diameter bores at right angles across the long dimension (Fig. 1). One of the bores is capped at both ends with high pressure sodalime glass windows (Type 62, $\frac{1}{4}$ " NPT, Herbert Industrieglas, Wuppertal Germany). These windows are pressure rated up to 15 MPa. During measurements, the high pressure windows are heated using Kapton heater strips (K005020C5-0009B, Watlow Australia, VIC, Australia), in order to prevent condensation of the evaporated sample water onto the inner walls of the windows. The second bore is plugged with a stainless steel cap at one end, and attached to a high pressure gas line at the other.

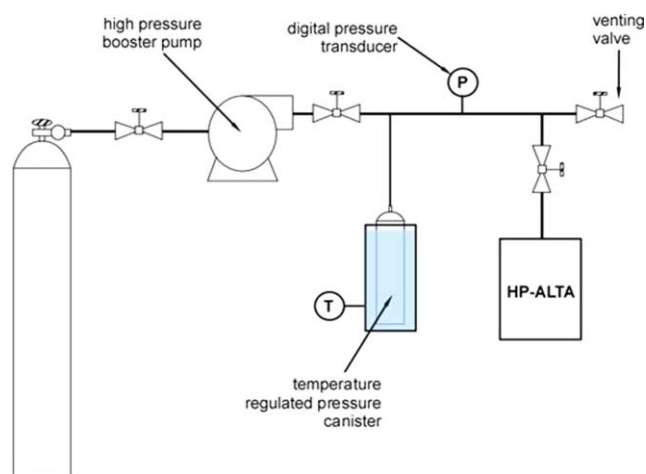


FIG. 2. (Color online) Schematic image of the high pressure gas line.

The pressure chamber is sandwiched between two Peltier devices (Peltier-CP1.4-127-06L-RTV, Melcor) of $\sim 40 \text{ mm} \times 40 \text{ mm}$ each, which in turn are sandwiched between two custom made aluminium heat sinks. The heat sinks have channels inside them so that they can be cooled using an appropriate coolant such as an alcohol or glycol. The coolant is cooled and circulated by an external refrigerated bath (Model WCR-P12, All-Lab Scientific). The HP-ALTA is also equipped with a thermocouple (PT100 HEL705, Honeywell) that is placed at a reference point in the chamber block, approximately 5 mm away from the right angle bores (the thermocouple is under ambient pressure). This thermocouple reading is output to a PC, which also allows feedback control of the current to the Peltier devices.

In order to guard against ambient temperature fluctuations which might influence gas pressure in the gas handling system during the lengthy automated measurements, a temperature controlled pressure canister was incorporated into the line (Fig. 2). The canister was immersed in a large temperature bath that maintained the temperature of the canister, and hence the gas pressure inside, constant. The size of the pressure canister was chosen so that the volume of the pressure canister was no smaller than 90% of the total volume of the line and the HP-ATLA.

The main gas line was connected to a pressure booster pump (Model AG-62, Haskel Australasia Pty Ltd, Queensland, Australia), enabling elevation of gas pressure up to 15 MPa. The pressure canister and HP-ALTA were isolated from the booster pump immediately prior to commencing measurements.

A white LED (NSPW500BS, Nichia Corporation) and a photo detector (BPV11, Vishay) are aligned so that the intensity of the transmitted light through the sample can be measured. The detector output was connected to the computer. The HP-ALTA setup is housed in a plastic case which is continually fed with a gentle stream of dry nitrogen in order to disperse ambient moisture.

Custom written software (Labview, version 8.5, National Instruments) is used to measure and control the temperature of the HP-ALTA using the thermocouple and Peltier inputs/outputs. The same software also records the light

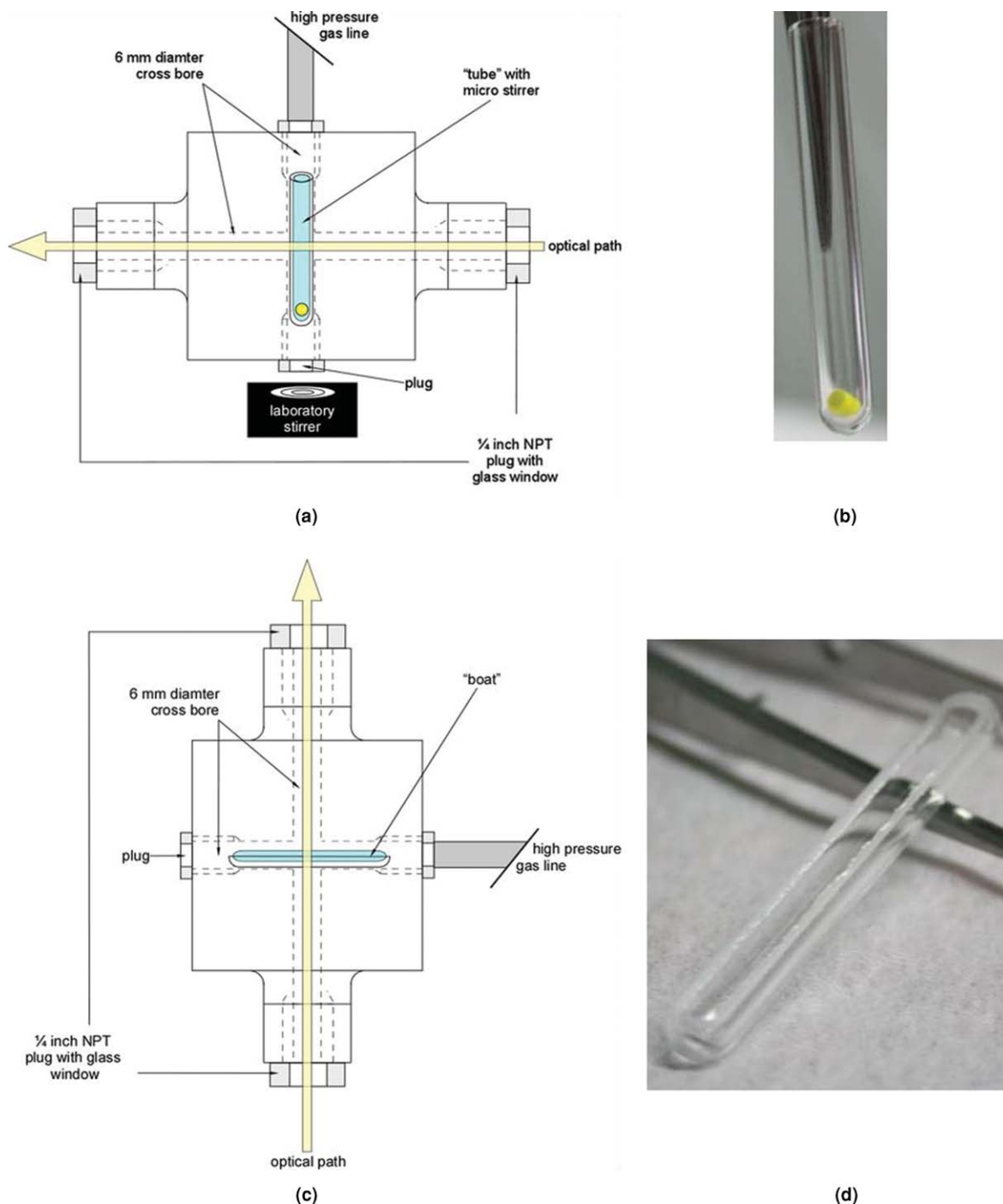


FIG. 3. (Color online) (a) HP-ALTA “bulk transmittance configuration” which uses a horizontal light path and custom made glass tube with a mini stirrer (b). (c) “interfacial transmittance configuration,” which uses a vertical light path and custom made glass boat (d).

intensity from the photodetector. This signal is also used as a trigger for temperature ramps, as described below.

A calibration factor which relates the thermocouple temperature response to the actual water sample temperature was derived from control experiments using a thermometer immersed in ethanol in the sample cell within the HP-ALTA sample chamber.

A second series of control experiments was used to ascertain the current required to ensure that the Peltier device maintained the temperature of the sample cell at a specified value. Within the physical constraints of this hardware (i.e.,

the heat capacity of the chamber and the power of the Peltier device), the instrument was able to cool the sample at a constant (linear) cooling rate in the range between 0.01 K/s and 0.075 K/s.

Detection of hydrate formation is based on the decrease in detected light intensity due to the increased scattering/absorbance of the hydrate relative to water.

We observe that during sample heating and cooling, transmittance of the light through the sample chamber drifts, presumably due to a combination of convection currents, and refractive index/electrical sensitivity variations. However, the

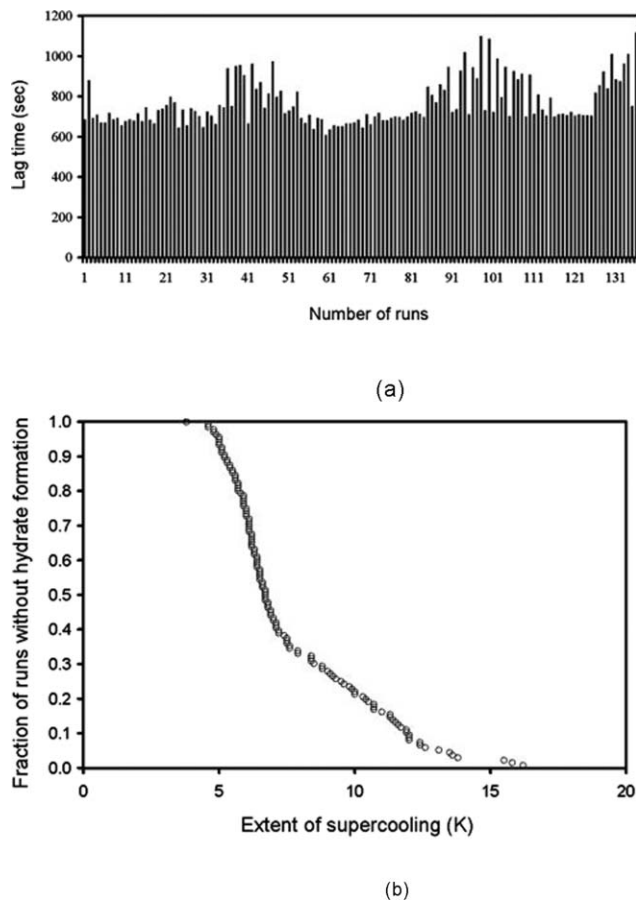


FIG. 4. Typical lag time histogram (a) and corresponding S-curve (b) data using the “bulk transmittance” configuration for a stirred water sample under 13 MPa of C1/C3 gas. The cooling rate was 0.025 K/s and the dissociation conditions after each cooling ramp was at 310 K for 300 s.

rate of decrease of transmittance on hydrate formation is far greater than this drift. Hence, the hydrate formation point is based on detection of a rapid decrease in transmittance, rather than on an absolute transmittance measurement.

The HP-ALTA thus cools a sample at a specified cooling rate in the aforementioned range until it detects formation of gas hydrates from a sudden reduction in the transmitted light through the sample. We refer to the formation temperature of gas hydrates as T_f . Following the detection of the formation of gas hydrates, the HP-ALTA then heats the sample to a defined temperature, ~ 10 – 15 K above the equilibrium dissociation temperature, T_{eq} , of the gas hydrate at the experimental pressure. Once this temperature is reached and the transmittance of the light through the sample has recovered to a high level (i.e., hydrate has largely dissociated), the sample temperature is maintained for a given time (typically 300 s) to ensure complete hydrate dissociation. After this time, sample cooling is again commenced, and the cycle repeated.

T_f for each cycle is recorded, resulting in a collection of varying T_f values in chronological order which can be displayed in the form of a histogram (so called “Manhattan”^{15,16}), as shown in Figs. 4 and 5.

Rearrangement of this data to present the fraction of hydrate formation events recorded at a given supercooled tem-

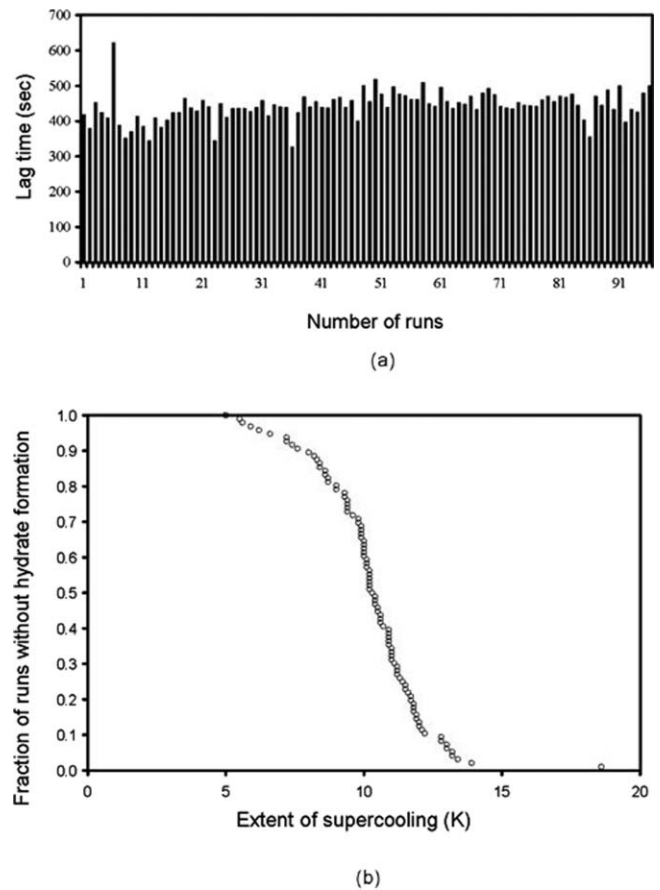


FIG. 5. Typical lag time histogram (a) and corresponding S-curve (b) data using the “interfacial transmittance” configuration for a quiescent water sample under 12 MPa of C1/C3 gas. The cooling rate was 0.05 K/s and the dissociation conditions after each cooling ramp was at 310 K for 300 s.

perature ($\Delta T \equiv T_{eq} - T_f$) allows depiction of the probability distribution for hydrate formation as a function of supercooling. This is the so-called survival curve or “S-curve”.^{15,16} An example is shown in Figs. 4 and 5.

The mid point of the S-curve denotes the ΔT value at which 50% of the measurements showed hydrate formation (median ΔT), and is denoted ΔT_{50} . This is a useful statistical value which can be used to compare S-curves recorded in different experimental conditions. A median is preferred to an average as the representative parameter, because an average is more susceptible to occasional spikes in these lengthy measurements.

In addition to the HP-ALTA described above, we built a second version of the instrument (which we refer to as HP-Video cell) to allow visualization of the changes that are occurring inside the HP-ALTA cell. The design of the HP-Video cell required the installation of a larger window (Type 62, $\frac{3}{4}$ ” NPT, Herbert Industrieglas, Wuppertal Germany), which in turn required some minor modifications to the design of the high pressure chamber block. The mass of this block was slightly more than the one for the HP-ALTA so there are some differences in the heat capacity. However, after careful calibration (similar to the HP-ALTA) it was possible to operate the instrument in the same range as HP-ALTA.

The dimension of the bore that accommodates the sample cell is the same as that for the HP-ALTA, so the same sample cell can be used in both the HP-ALTA and the HP-Video cell. The heat sinks, the thermocouple, the electronics, and the computer software are the same as those of the HP-ALTA; however, the optics is different. The LED of the HP-ALTA was replaced with a flexible and adjustable light guide (CL 1500 EC Cold light source, Carl Zeiss Pty Ltd, Australia) and the photo detector of the HP-ALTA was replaced with a video camera (CMA-DICE, Sony). The video image was recorded with a DVD recorder (DVR-540H, Pioneer).

III. DESIGN CONSIDERATIONS OF HP-ALTA RELATIVE TO AMBIENT PRESSURE ALTA

The ambient pressure ALTA of Haymet, Heneghan and Wilson^{16,17} was designed to study nucleation of ice and THF hydrate systems. In these systems, nucleation and growth of hydrate are essentially simultaneous, because formation is the result of a phase transition either from a one component system (water \rightarrow ice), or from a mutually miscible two component system (THF + Water \rightarrow THF hydrate). The ambient pressure ALTA therefore detects this phase transition by a reduction in light transmittance through the bulk of the sample.

The situation for gas hydrate nucleation is somewhat different, since the initial gas and water components are sparingly miscible. Nucleation of hydrate therefore occurs at the gas-water interface. Furthermore, growth of hydrate into the bulk water phase requires transport of one component through another (e.g., gas dissolution and diffusion through hydrate or water), which is generally slow.¹⁸

To adapt the ambient ALTA to study gas hydrate nucleation therefore, it is necessary to either facilitate gas transport by mixing, or to focus the detection system at the gas-water interface. Both approaches were explored in the development of the HP ALTA.

A. Approach 1: Stirred tube/bulk transmittance configuration

The ambient ALTA tube configuration was adapted for use at high pressure in conjunction with a stirring action (Fig. 3). Here a small micro stirrer (Spin bar magnetic flea, F371210009, Crown Scientific, Minto, NSW, Australia) was placed inside the sample tube. One or more small glass spheres (1.5–2 mm, 332134Y, BDH Laboratory Supplies, Poole, UK) were also placed at the bottom of the sample tube (and below the stirrer) to increase the stirring agitation. The stirrer was driven by a common laboratory stirrer plate which was placed beneath the HP-ALTA cell. Using this configuration, the stirring action was effective in allowing the detection of gas hydrate in the bulk water sample, as determined by measurable reductions in bulk transmittance during cooling ramps. However, introduction of the stirring action requires consideration of a number of additional parameters such as stirring efficiency, and stirrer position relative to the detection light path and/or water-gas interface. The necessity for specifying and characterizing these additional

parameters complicates the measurements significantly; however the fact that this configuration allows determination of “S curves” in a dynamic environment is of interest in some situations.

B. Approach 2: Static sample/interfacial transmittance configuration

A simpler approach was to measure formation of gas hydrates at the gas water interface by adapting the light path to pass through this interface. This required rotating the light path by 90°, and replacing a tube in the ambient pressure ALTA with a customized glass sample cell or “boat” (Fig. 3). The “boat” exposes a larger area of the water surface to the gas (~ 7 mm² in the tube configuration and 90 mm² in the boat configuration). This configuration precludes the use of a micro stirrer (the stirrer could not rotate in the boat). As such, only measurements of quiescent (static) samples could be carried out in the boat configuration.

This is the preferred configuration of the HP-ALTA system, since it reduces the experimental complexities relative to the stirred tube configuration described above.

IV. OPERATION OF THE HP-ALTA INSTRUMENT

A. Approach 1: Bulk transmittance configuration

To perform the measurements, approximately 170 μ l of milli-Q water is placed in a custom made cylindrical glass tube, which is inserted into the vertical pressure chamber bore. Light is passed horizontally through the bulk of the sample water, ~ 13 mm above the bottom of the tube, and ~ 7 mm below the gas-water interface. The surface area of the sample water that is exposed to the high pressure gas is ~ 7 mm².

Once the sample cell is in place, the high pressure gas line is connected to the HP-ALTA using a Swagelok connector (SS-400-1-2, Swagelok, Broadmeadows, Australia). The gas cylinder regulator is opened and the pressure booster pump is operated to pressurize the gas line to a desired value. Different types of gases and gas mixtures can be studied using pressure handling system; however, we describe below the case for a 90% methane-10% propane (C1/C3) gas mixture only.

While the gas pressure in the system stabilizes, the refrigerated bath is switched on and the temperature is set to a desired value, based on the Peltier device operating capacity and the desired temperature range to be studied. In general, the refrigerated bath temperature should be set close to the lowest temperature that may be required for the nucleation of gas hydrates in a given experiment. The window heater is switched on in order to eliminate condensation. The electronics and the computer are switched on and the program is activated. At this point, the gas cylinder is isolated from the pressure line, and the pressure booster pump is switched off for safety reasons. Pressure transducers in the pressure line allow checking for (and elimination of) gas leaks, and allow checking that a stable pressure is maintained in the system for the duration of the measurements. The first Peltier temperature ramp is then initiated, and measurements are commenced as described above.

Figure 4 shows the typical “Manhattan” histogram data and corresponding S-curve for gas hydrate nucleation in a stirred water sample that was exposed to C1/C3 gas mixture under 13 MPa pressure. The cooling rate was 0.025 K/s and the sample was heated at 310 K for 300 s after each cooling ramp to dissociate the gas hydrate which was formed. It can be seen that C1/C3 gas hydrate was formed at supercooling temperatures (ΔT) of 4–17 K below the equilibrium hydrate dissociation temperature, T_{eq} , of 296 K, which was calculated using CSM Gem software for this system.⁹ The median ΔT (ΔT_{50}) for this system was determined to be 7 K.

Compared with the S-curve data for unstirred ice nucleation at ambient pressure,^{15,16} the S-curve here is less symmetric. This difference may be arising from the multi-component nature of the gas hydrate systems studied here.

B. Approach 2: Interfacial transmittance configuration

As described above, a second configuration of the HP-ALTA allows monitoring of the gas-water interface where the initial nucleation and growth of gas hydrates occurs.

We manufactured different types of glass boats before settling to the final design. In general, a design that resulted in exposure of a larger surface area of the sample water led to a somewhat higher T_f with a narrower distribution. However, it also led to accelerated evaporation of the sample water, especially during the heating (dissociation) process. This gradual depletion of water from the sample limits the experimental run length to ~ 1 week. For an optimal cooling rate of 0.025 K/s, this corresponds to ≈ 230 cooling-heating cycles.

To perform the measurements, approximately 130 μl of milli-Q water is placed in a custom made glass boat, which is inserted into the horizontal pressure chamber bore. Light is passed vertically through the gas-water interface. The rest of the operation procedure is similar to that described for the bulk transmittance configuration described above.

Figure 5 shows the typical “Manhattan” histogram data and corresponding S-curve for gas hydrate nucleation in a water sample that was exposed to C1/C3 gas mixture under 12 MPa pressure. The cooling rate was 0.05 K/s and the sample was heated at 310 K for 300 s after each cooling ramp to dissociate the gas hydrate which was formed. It can be seen that C1/C3 gas hydrate was formed at supercooling temperatures of 5–19 K below the equilibrium hydrate dissociation temperature, T_{eq} , of 296 K. The median of ΔT (ΔT_{50}) was about 10 K. The range of subcooling observed is similar to that found using the bulk transmittance (stirred) configuration.

We found variations in ΔT_{50} for different samples in different glass sample cells (data not shown). Direct visual inspection of the sample using the HP-Video cell revealed that the nucleation of gas hydrates typically occurred at the edge of the cell and that this was followed by growth of a hydrate layer across the interface (Fig. 6). We note that the instrument cannot directly detect the formation of (sub-microscopic) nucleus. Our hypothesis is that once the gas hydrates nucleate somewhere in the sample cell, it will readily lead to the

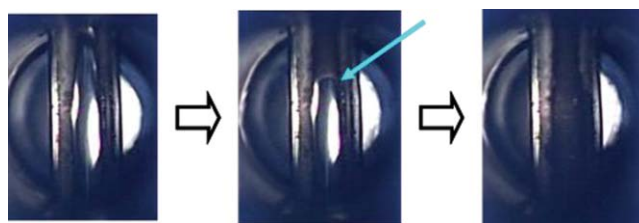


FIG. 6. (Color online) An example of direct visual inspection of the sample through one of the high pressure windows. Direct visual inspection revealed that the nucleation of gas hydrates typically occurred from one of the edges of the boat and that the gas hydrate grew across the rest of the interface. The blue arrow in the middle panel shows the position of the hydrate growth front.

growth of the gas hydrates. For the “interfacial transmittance configuration” it is assumed that the nucleation of gas hydrates would lead to subsequent growth of the film over the entire surface, as illustrated in Fig. 6. The growth rate of such film was not instantaneous. However, the cooling rate used was slow (typically 0.025 K/s) so that a small delay in the detection of the formation of gas hydrates due to the finite speed of the film growth would not translate to a large error in the lag time (< 1 K).

The variation in T_f among different samples (in different glass cells) may arise due to minute differences of the glass-water-gas three phase contact line for each cell due to scratches or defects in the cell wall which influences the heterogeneous nucleation process. We hypothesize that this results in variations in nucleation probability for different cells. We note that supercooling has been shown to increase, and hydrate nucleation becomes more stochastic, for smaller sample volumes.¹⁹ Given that the sample volume we employ in the HP-ALTA is much smaller than in any other measurement system, the rather large range of supercooling we observed in the HP-ALTA is not surprising.

V. CONCLUSIONS

A novel method of studying nucleation and growth statistics of gas hydrates, HP-ALTA, was developed that could be operated in multiple configurations. A large (> 100) number of nucleation and growth events could be collected automatically for a given sample under controlled pressure-temperature conditions. The “bulk transmittance configuration” detects hydrate formation in bulk in conjunction with stirring action. In contrast, the “interfacial transmittance configuration” detects formation of hydrate films at the water-gas interface. The range of supercooling detected was very similar between the two configurations for 12–13 MPa of 90% methane-10% propane (C1/C3) gas mixture. The median of the data set, ΔT_{50} , was also similar between the two configurations. The median and the range provide a quantitative measure of the probability distribution for hydrate nucleation and growth in a gas-pressurized water sample under supercooled conditions. The shape of the distribution can provide additional insight as to whether more than one process may be taking place. Such insight would be difficult to obtain using a system where the measurement is only made a few times. The technique can be applied for the study of the effect of several

parameters on ΔT_{50} , such as gas pressure, cooling rate and gas composition.

ACKNOWLEDGMENTS

This work was supported by CSIRO's Petroleum and Geothermal Research Portfolio, Chevron Energy Technology Company, and British Petroleum. In addition, N.M. acknowledges the support of an Australian Research Council Future Fellowship (FT0991892). The authors also thank Ramesh Kini, Ravi Gudimetla, Adam L. Ballard, and Richard G. Chapman for helpful discussions.

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