

A NEW METHOD FOR THE STATISTICAL EVALUATION OF NATURAL GAS HYDRATE NUCLEATION AT ELEVATED PRESSURE

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ABSTRACT

Nucleation is a stochastic process, most accurately represented by a probability distribution. Obtaining sufficient data to define this probability distribution is a laborious process. Here, we describe a novel instrument capable of the automated determination of hydrate nucleation probability under non-equilibrium conditions for a range of natural gas mixtures at pressures up to 10MPa. The instrument is based on the automated lag time apparatus (ALTA) which was developed to study the stochastic nature of nucleation in ambient pressure systems [1]. We demonstrate that the probability distribution represents a robust and reproducible tool for the quantitative evaluation of hydrate formation risk under pseudo-realistic pressure conditions.

Keywords: gas hydrates, nucleation, super-cooling, sub-cooling.

INTRODUCTION

Gas hydrates commonly form in sub-sea oil and gas pipelines at high pressure and low temperature. The hydrates are problematic because they can grow to form plugs that completely block the pipes and prevent the flow of production fluids. Remediation can be time consuming and costly.

Oil & gas production facilities are designed and constructed to minimise any risk of hydrate formation. Operational procedures include strategies for hydrate prevention and mitigation such as the addition of thermodynamic or kinetic inhibitors. However, better understanding of the hydrate risk factors will help engineers to design and operate their facilities to tighter margins at considerable cost savings.

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When a hydrate forming system reaches a temperature and pressure at which hydrate formation is possible, there is a delay (induction time) before hydrate formation is actually observed [2]. Since nucleation is a stochastic process, the exact induction time will be different for each experiment, even if all conditions remain identical. Many measurements are therefore required to obtain a statistically valid probability distribution of results.

Due to the high pressures required for the formation of natural gas hydrates, large pressure vessels are needed to withstand the pressures involved. These vessels have a large thermal mass, so dynamic experiments are difficult due to the significant temperature lags involved. Most experiments are carried out at isothermal temperatures, but induction times can be extremely long, so it is time consuming to undertake many repetitions at the same experimental conditions.

To overcome some of these problems, model hydrate systems (such as THF) are often studied in preference [2,3]. However, the model compounds do not necessarily behave in exactly the same way as natural gas hydrates in pipe lines at pressure, so researchers were keen to find a way to study the nucleation of natural gas hydrates, at pressure in a statistically valid way.

In the 1990's Haymet, Heneghan and Wilson developed and refined an instrument that is able to measure the nucleation of ice at ambient pressures [1]. This instrument is known as the Automatic Lag Time Apparatus (ALTA) and has been successfully applied to the study of THF/water hydrates at ambient pressures [4].

The instrument relies on the fact that liquid water becomes somewhat opaque on freezing. By monitoring the intensity of a light beam through the sample cell it is possible to detect this freezing event by a sudden drop in light intensity. A similar change is observed during the formation of THF/water hydrates.

A small liquid sample (approx 300 μ L) in a custom made sample tube (similar to an NMR tube) is placed into an aluminium block. The temperature of the block is accurately controlled by a couple of peltier cells and heat sinks. The small volume of the sample allows rapid heating and cooling at a

well controlled rate, with minimal thermal lag. Current to the peltiers is controlled by a computer interface. The temperature of the block is linearly cooled at a known cooling rate (α) until a freezing event is detected. The temperature recorded for this event is always lower than the equilibrium formation temperature and is known as the degree of sub-cooling or super-cooling. In ALTA experiments it is referred to as ΔT_{50} and is defined as the temperature at which 50% of the sample runs recorded a freezing event, relative to the equilibrium formation temperature.

Haymet and co-workers were able to demonstrate that sufficient data points were collected during each experiment to produce a nucleation probability distribution function for a specific set of experimental conditions. They were also able to demonstrate that the results obtained were independent of cooling rate [1]. Changing the experimental conditions (for example by addition of an impurity) shifted the probability distribution to a smaller super-cooled value (i.e. nucleation was able to occur at smaller magnitudes of supercooling) [4].

Having demonstrated that the instrument was effective for measuring ice nucleation and THF hydrate nucleation, the next logical step was to extend the technique to study the nucleation of natural gas hydrates formed at elevated pressures. With careful redesign of the sample chamber, alteration to some electronic and thermal controls and modification of the instrument software, a new version of the instrument was born. The new instrument was named the High Pressure Automatic Lag Time Apparatus (HP ALTA).

Unlike other pressure instruments, the HP ALTA is able to generate indicative results for a particular hydrate system within minutes, a good probability distribution within a day (results accurate to within one degree) and a statistically robust data set in 2-3 days. The instrument is relatively small and compact (bench top) and allows the operator to control important parameters such as melting temperature, hold time and cooling rate.

EXPERIMENTAL DETAIL

All measurements described here were made with a purpose built automated nucleation device, which we have named as the high pressure automated lag time apparatus (HP ALTA). The water used in these experiments is sourced from a Millipore ultra pure water system (model ZAMQ05001). Feedstock for this system is deionised house supply lab water (treated by ion exchange then activated carbon filtration). The conductivity of the purified water is indicated on the purifier as $<20 \text{ MS/cm}$ ($1\text{S} = 1 \text{ Ohm}^{-1}$).

Sample cells are custom made from borosilicate glass tubing with an external diameter of 4mm and an internal diameter of 2mm. Before their first use, these cells were cleaned in chromic acid to ensure that the surfaces were free of any contamination. Each sample cell holds approximately $100\mu\text{L}$ of water during an experiment.

The gas used is a custom mixture of 90% methane/10% propane, obtained from BOC Gases. The purity of this gas is 99.99%.

At the start of each experiment, a sample tube containing $100\mu\text{L}$ of water is placed into the high pressure cell. The cell is then sealed and flushed several times with the gas mixture to displace any air present. The pressure is then carefully increased to the desired pressure (maximum working pressure is 10MPa). At this point the lines are sealed and the cylinder is closed. Pressure losses from the system over a period of 3-5 days are minimal (no greater than 0.1 MPa).

The sample cell is then held at a temperature (above the equilibrium hydrate formation temperature for the experimental pressure used) for a defined period of time. The temperature of the cell is then linearly cooled (at a defined cooling rate) until nucleation is detected. The peltiers then switch to heating mode and raise the temperature back to the original value, where it remains for a defined period of time (to ensure complete melting of the sample). The cycle then begins again and is repeated as many times as desired to produce a statistically valid data set (generally 300 data points, but at least 160 data points).

Information is recorded in a computer data file for later processing.

RESULTS AND DISCUSSION

When the data is processed, several graphs are produced to evaluate the quality of the information. The first graph is a plot of “lag time” vs run number, which was referred to as a “Manhattan” by Haymet and co-workers. A typical example is given in Figure 1.

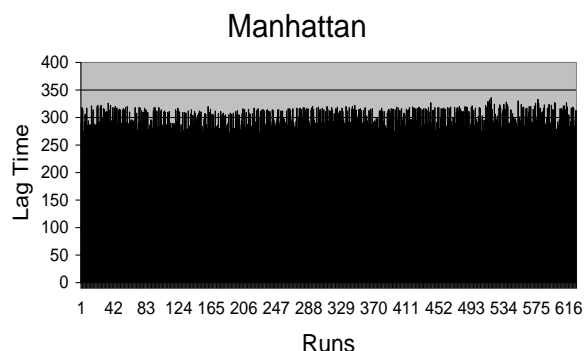


Figure 1. Typical HP ALTA “Lag Time” Data.

The lag time is the number of seconds recorded on the linear cooling ramp since the temperature passed through the equilibrium formation temperature. Since the cooling rate is known, the lag time can easily be converted to temperature (and vice versa). The Manhattan graph gives a visual assessment of the data quality. The lag time would be expected to vary from run to run, but remain relatively consistent across the duration of the experiment. A drift in the lag time data (increasing or decreasing with run number) would indicate a systematic variation during the experiment (for example, clouding of the detector or light source). An extremely scattered or variable Manhattan or a sudden change in lag time might indicate the presence of a bubble (or particle) in the light beam.

The second graph that is produced is a “survival curve” which plots the fraction of samples that remain unfrozen as a function of sub-cooling (ie the temperature of the detected freezing event relative to the equilibrium formation temperature). A typical example is given in Figure 2.

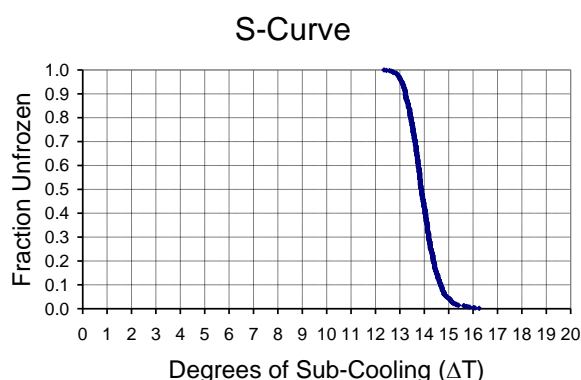


Figure 2. Typical “S-Curve”

It was important to establish that gas hydrates were formed within the instrument, not simply ice, so a number of experiments were run at different pressures to investigate.

Under equilibrium conditions and ambient pressure, ice can form at 273K. In the HP ALTA (cell left open to the atmosphere at ambient pressure), a sub-cooling of approximately 14°C is obtained for ice nucleation (ie a freezing event is detected by the instrument at around 259K).

When the cell was sealed and flushed with the 90% methane/ 10% propane gas mixture at pressures ranging from 3.0 to 4.7MPa, freezing events were detected in the range 273K to 280K – i.e. above the equilibrium freezing point of water.

The phase diagram for ice formation shows that the equilibrium formation temperature *decreases* at higher pressures, and would equate to a decrease of approximately 0.6K over the working pressure range of the HP ALTA (0 to 10MPa). It is therefore reasonable to assume that pressure will have a negligible effect on the super-cooling temperature of ice formation in this instrument.

The equilibrium formation temperature for hydrate formation from this particular gas composition is calculated to *increase* with pressure by 22.5K over the range 0.5 to 10MPa.

The freezing events that we detect in the HP ATLA at pressure using the methane/propane gas mix occur at temperatures above the equilibrium formation temperature of ice and seem to occur at

higher temperatures for higher pressures (in general). Table 1 shows some typical results obtained to date. The data is grouped together into boxes to indicate experiments where all variables were constant (i.e. same sample tube, same water sample, same instrumental settings).

Since this data was collected, further improvements have been made to the instrument to control the temperature of the sample, calibrate for thermal lags within the instrument and define the optimum settings for future experiments. Now that this is complete, the experiments shown in Table 1 will be repeated. However, the most logical conclusion from the data presented is that gas hydrates are formed and detected by the HP ALTA instrument.

Sample Date	Pressure (MPa)	ΔT_{50} (°C)	Freezing Event (K)
12 th Jan	4.70	11.67	279.3
15 th Jan	4.50	12.11	278.6
16 th Jan	3.50	13.92	274.9
23 rd Jan	3.15	17.35	270.2
10 th May	4.10	14.68	275.3
9 th May	4.10	14.09	275.9
4 th May	3.00	13.42	274.1
3 rd May	3.00	13.13	274.4
7 th May	2.30	10.21	274.8
25 th May	4.00	12.72	277.3
28 th May	4.00	12.09	277.9
1 st June	3.00	14.62	272.9
24 th May	3.00	13.40	274.1
18 th June	3.60	15.77	272.7
22 nd June	3.00	12.01	275.5

Table 1. Hydrate Nucleation as a Function of Pressure.

In order to determine the reproducibility of the experiments and the number of experiments required to give a reasonable estimate of ΔT_{50} , the long experiment shown in Figures 1 and 2 was divided into data sub-sets and reanalysed. Results are shown in Figure 3 and Table 2.

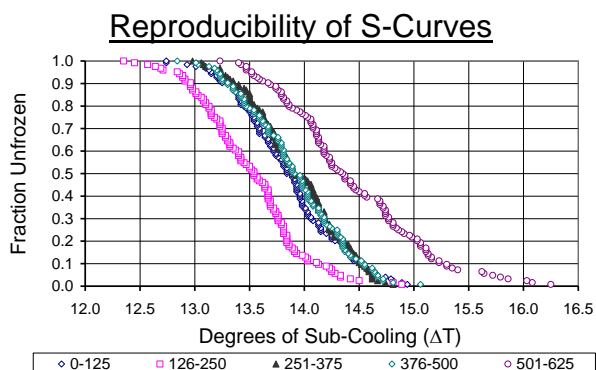


Figure 3. Reproducibility of Data within One Experiment of 625 Runs

Run	ΔT_{50} (°C)	ΔT_{95} (°C)
0-125	13.84	13.20
125-250	13.54	12.84
250-375	13.91	13.20
375-500	13.91	13.20
500-625	14.35	13.52
0-625	13.89	13.08

Table 2. Reproducibility of Data within One Experiment of 625 Runs

The data shows that even data sets as short as 125 runs will give an estimate of ΔT_{50} within 0.5 of a degree and all results fall within a range of approximately 4 degrees.

Previous work by Haymet and Wilson [4] has shown that differences in sample cell alone can shift the value of ΔT_{50} by up to 3 degrees (which is most likely due to surface defects in the glass which may assist the nucleation process to varying degrees). Addition of sand or rust can shift the value of ΔT_{50} by as much as 7 or 8 degrees, so this instrument will therefore be able to confidently monitor changes to the nucleation process from different factors (e.g. pressure, composition and impurities), if the sub-cooling is altered by more than a degree or two.

CONCLUSIONS

The HP ALTA instrument is able to detect hydrate nucleation in typical natural gas hydrate mixtures

at elevated pressures. The data produced is extremely similar to previous ambient versions of the instrument and reproducibility within one extended run is good.

The HP ALTA instrument will therefore be a robust method for detecting significant changes in hydrate nucleation as a function of different experimental parameters in the future which may include cooling rate, pressure, addition of an impurity, gas composition and liquid composition.

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