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# Experimental Evidence of Gas Hydrates Dissociation Kinetics by Shifting their Equilibrium Conditions

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**Abstract.** The scope of this study is to define the rates under which multi-component gas hydrates contained in the pore space of a mud volcanos' (MV) sediments may decompose in gas and water phase as a result of pressure decrease or temperature increase. Such cases can be encountered during retrieval and handling of pristine samples from the sea floor, or due to an increase of hot mud fluxes from underneath the MV area. Both of the aforementioned shifts of conditions have been studied in the bulk liquid phase of a reactor, while pressure decrease has also been studied in a piston vessel containing artificial sediment at the Centre for Gas Hydrates Research, HW University, Edinburgh.

The results indicate that gas hydrate dissociation progresses much faster with pressure decrease than with temperature increase. Moreover, depressurization at temperatures above 15°C causes higher dissociation rates in comparison to that at lower temperatures.

## 1. Introduction

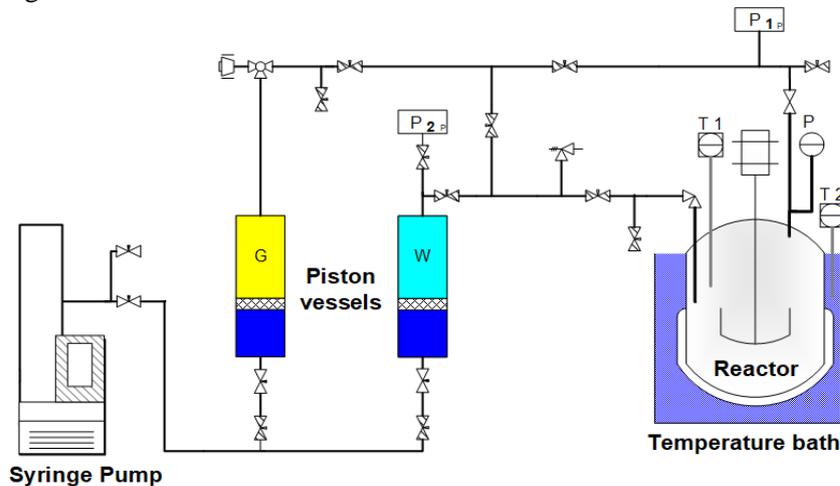
Gas hydrates are crystalline compounds which can be formed when water or ice and suitably sized molecules, such as the ones of natural gas, are brought together under favorable conditions. Despite their resemblance to common ice they contain substantial amounts of natural gas (175 Nm<sup>3</sup> of gas per m<sup>3</sup> of gas hydrate). The pressure-temperature conditions for their formation depend mainly on the composition of the gas and of the water-rich phase and they can be found in the oil/gas transmission pipelines and in the natural environment of permafrost regions and deep water geological formations.

While both single and multi-component natural gas can be enclathrated in the hydrate phase in natural environments, the up-to-date research on the stability of the hydrate reserves focuses primarily on single gas component hydrates. When hydrates contain several gas components there is a range of dissociation pressures for any given temperature instead of a single one with the lower limit depending on the initial vapor composition, while the upper limit is almost identical to the pure methane hydrate's dissociation pressure [1]. Such hydrate formation conditions prevail at the "Amsterdam" mud volcano, the most prominent mud volcano in the Anaximander Sea Mountains, and possibly the largest in the Eastern Mediterranean [2]. Sediments containing multicomponent gas hydrates were retrieved at an average depth of 2000m below sea level and at water temperatures of 12-14°C [2-3]. The behavior of the gas hydrates in this area was experimentally simulated using a ternary gas mixture (77% methane, 15% ethane and 8% propane) along the conditions that the recovered pristine sample will be exposed at from the sea bed to the surface and during transportation to the lab.



## 2. Experimental Setup

The experimental setup that was used for studying the dissociation kinetics is schematically presented in figure 1.



**Figure 1.** Experimental setup used for gas hydrate decomposition kinetics tests.

A Syringe Pump is connected to a cylinder with the gas mixture and to a cylinder which contains de-ionized water that has been degassed under vacuum. Both cylinders are connected to a 100ml volume PARR reactor, equipped with magnetic stirrer. The reactor is housed in a refrigerated bath and the temperature and the pressure of the reactor are measured and logged to a computer [4].

## 3. Hydrate decomposition procedure

The decomposition of the GH in the reactor system was studied in one of the following two ways:

1. The system pressure was reduced in a single step to a value much lower than the hydrate stability limit, while stirring at 900 rpm at different constant bath temperatures (2.5 to 30°C). The volume change, pressure and temperature of the water in the reactor were monitored during decomposition.
2. The system was heated from the initial formation temperature up to 30°C, where all hydrates were expected to decompose at constant pressures and at high stirring rates. Pressure, volume change and temperature of the water in the reactor are monitored.

The results from the aforementioned experiments are presented in two sets of graphs. The first set (figures 2, 4a, 5a and 6) displays the normalized increase of the volume of the system, which is produced from the hydrates dissociation and the expansion of the gas with time:

$$\frac{P_t \cdot (V_t - V_{t=0})}{P_{t \rightarrow \infty} \cdot (V_{t \rightarrow \infty} - V_{t=0})} \quad (1)$$

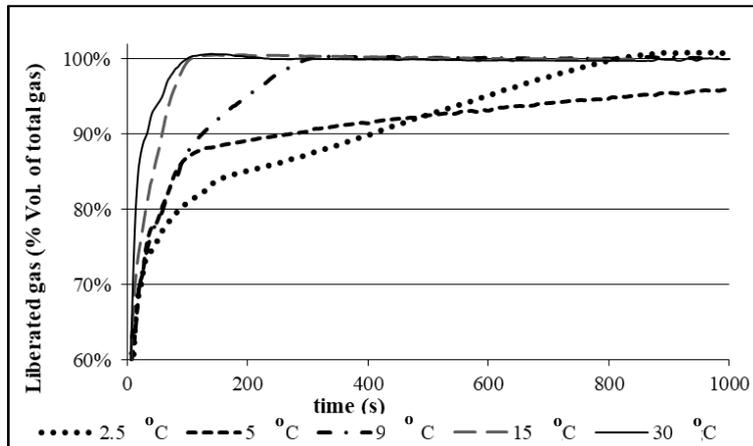
Where  $P_t$  and  $V_t$  are the system pressure and volume  $t$  seconds after decomposition begins,  $P_{t \rightarrow \infty}$  and  $V_{t \rightarrow \infty}$  are the final pressure and volume of the system after decomposition and  $V_{t=0}$  is the initial volume of the system.

The second set (figures 3, 4b and 5b), displays the temperature difference between the bath and the reactor with time, during decomposition. It can be used for evaluating indirectly the GH dissociation rate as the higher the dissociation rate, the steeper the temperature drop of the system. The area between the temperature variation curve and the time axis is proportional to the amount of heat that was consumed by the system for hydrates to be dissociated.

## 4. Results

### 4.1. Depressurization from 20 MPa down to 1 MPa at different constant bath temperatures.

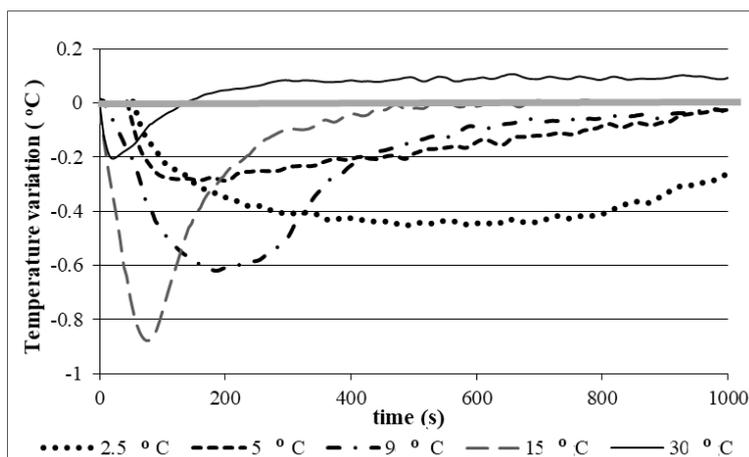
Figure 2 displays the gas production with time, while the temperature variation between the reactor and the cooling bath, as a result of GH dissociation (endothermic reaction), is shown in figure 3.



**Figure 2.** Normalized volume increase during depressurization down to 1 MPa at constant bath temperature (2.5-30 °C).

From figure 2 it is concluded that the GH dissociation rate during depressurization under stirring is very fast. The dissociation rate increases slightly with temperature. If  $t_{50\%}$  and  $t_{90\%}$  are the times required for the dissociation of 50% and 90% of the gas hydrates contained in the experimental system respectively, then  $t_{50\%}$  is less than 7 sec for any temperature, while  $t_{90\%}$  decreases from 400 sec at 2.5°C down to 30 sec at 30°C. The curves at 15°C and 30°C are almost identical indicating that heat transfer is not a limiting factor for hydrate dissociation. As expected, the GH dissociation rates during depressurization decrease with temperature. Consequently, keeping GH pristine samples close to 2°C minimizes the risk of dissociation in case of sudden depressurization and avoid the risk of ice formation.

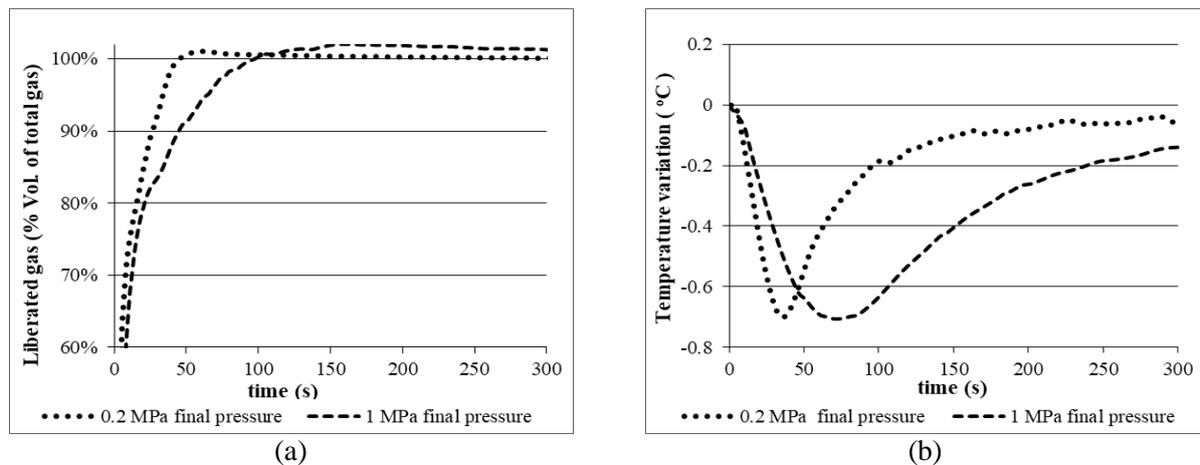
Figure 3 shows clearly that although the volume of the system increases at approximately the same rate for the temperature range of 15-30°C (figure 2), hydrates seem to exist only at temperatures below 20°C, as anticipated from the phase behaviour study. Over 20°C, the observed temperature drop is too small to account for hydrate dissociation. At 30°C, the volume increase is attributed solely to the free gas phase expansion in the system. The temperature drop is steeper as temperature rises, which implies that the volume increase is not a very accurate index for measuring dissociation rates when these rates are very high.



**Figure 3.** Temperature difference ( $T_{\text{reactor}} - T_{\text{bath}}$ ) due to GH dissociation during depressurization down to 1 MPa at constant bath temperature (2.5-30 °C).

The conclusion that can be drawn is that gas production under these conditions is a very fast process. The maximum production rate occurs during the first 10-20 seconds after the pressure is reduced down to 1 MPa for any temperature between 2.5-15°C. Consequently, using only the gas production rate measurements is not sufficient for determining the GH dissociation rates.

#### 4.2. Depressurization from 20 MPa down to 1 and 0.2MPa at constant bath temperatures.

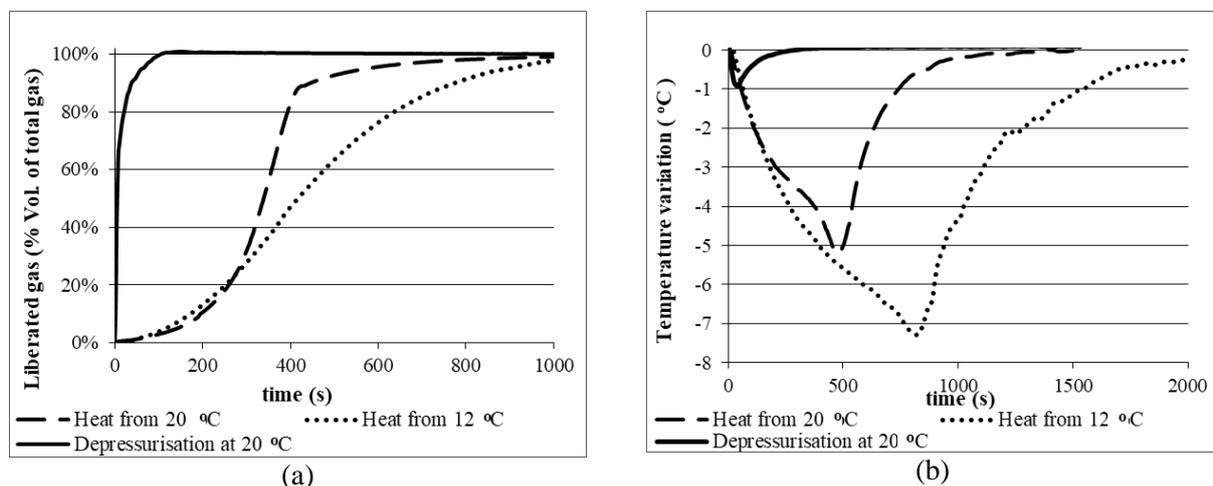


**Figure 4.** Comparison of the volume increase (a) and temperature drop (b) during depressurization from 20MPa, down to 1 and to 0.2 MPa final pressures at constant bath temperature.

In order to validate the impact of the final pressure on the dissociation rate, a test was conducted at 13°C and down to 0.2MPa. The results are presented in figures 4 (a) and (b) against similar measurements at 13°C and 1MPa final pressure. In figure 4a, it is shown that the final pressure does affect the dissociation rate. Although for both 0.2 and 1MPa final pressures,  $t_{50\%} \approx 6$  sec,  $t_{90\%}$  becomes 45 sec and 25 sec respectively.

#### 4.3. Gas hydrates dissociation during heating at constant pressure.

A second set of experiments was conducted by heating the gas hydrates at constant pressure of 20MPa and at 900 rpm stirring rates. The results are presented in figures 5a and 5b and for comparison the results of depressurization at 20°C are also presented.

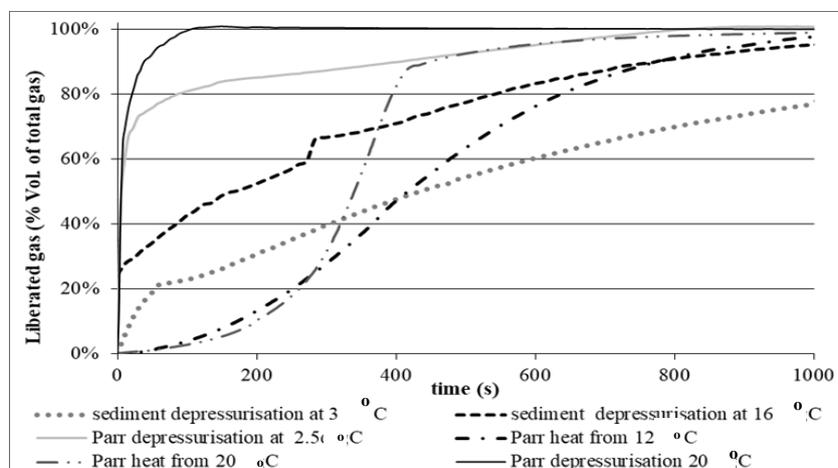


**Figure 5.** Comparison of the volume increase (a) and temperature drop (b) during heating up to 30°C at constant pressure (20MPa) and depressurization down to 1MPa at constant bath temperature (20°C).

#### 4.4. Dissociation of GH hosted in porous media by depressurization.

The results from this study were compared against measurements from another dissociation study performed by depressurizing GH formed from a multicomponent gas (81.95% C1, 9.5% C2, 3.5% C3, 1.9% C4, 0.65% C5, 1% CO<sub>2</sub> and 1.5% N<sub>2</sub>) and hosted in artificial sediment (glass beads 0.1 mm diameter) [5]. It is concluded that the GH decomposition rates in the sediment fall in between the ones during depressurization and during heating the reactor. This can be explained by the following:

- At the initial stage of GH decomposition, the required heat is provided by the host sediment
- Later on extra heat needs to be transferred to the sediment to sustain decomposition, otherwise the dissociation rates decreases.



**Figure 6.** Comparison of the GH decomposition results in the Parr reactor setup against results from GH decomposition contained in artificial sediment during depressurization at constant bath temperature.

## 5. Conclusions

- GH decomposition during depressurization in vessels with stirring is a very fast process. Temperature variations between the system and the heat tank are more accurate indicators for measuring dissociation rate differences than gas production volumes.
- GH decomposition during heating at constant pressure is a slow process. It depends on the heat transport rates and on the thermal inertia of the system.
- GH decomposition rates in artificial sediments during depressurization progresses initially as the ones during depressurization in a vessel, whereas later it approaches more to the rates observed during isobaric heating.

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