Gas hydrates are solid crystalline structures consisting of gas molecules surrounded by a cage of water molecules and are formed under low temperature and high pressure conditions. The study, and understanding of these materials is important in the following fields:

- **Flow assurance:** in both gas transportation and oil exploration gas hydrate formation can form blockages and catastrophic events. It is important to prevent the formation of hydrates and ensure optimal operational conditions.
- **Energy:** Potential exploration of gas hydrate deposits as an energy source.
  - Gas storage and transport: Selective formation of hydrates as a stable and efficient transportation mechanism for gas.
- **Water purification:** use of gas hydrates for desalination and production of drinking water.
- **Formation of selective hydrates** for CO2 capture and sequestration.

The determination of the thermodynamic properties and the kinetics of gas hydrate formation/dissociation are needed and therefore High Pressure DSC is required, using a specific gas tight controlled pressure vessel to enable precise control of pressure and temperature together with truly representative samples.

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The MicroDSC technology enables both the study of samples up to a volume of 1cc and controlled elevated pressures up to 1000bar. The MicroDSC uses a Calvet based calorimetry detector that consists of symmetrical peltier detectors located within a thermostated bulky calorimetric block that fully surrounding the experimental vessels (figure 1). The minimum temperature that can be reached is -45°C, and the maximum temperature is 120°C.

Figure 1: Cross section of the detector and the calorimeter

The gas tight high pressure vessel (figure 2) is available in both 400 and 1000 bar and contains 0.5 ml of sample. Because only the vessel, and not the entire calorimetry detector are pressurized the pressure and gas nature do not impact the calibration and performance of the detector.

The vessels are Hastelloy C276, which allows the analysis of corrosive fluids such as drilling fluids. The vessels are placed inside the calorimetric block and are connected to a gas high pressure panel (figure 2) including a one-stage compressor. The gas panel is designed to purge the vessels under inert gas, measure the pressure of reacting gas, apply, control and monitor the pressure inside the experimental vessels. The gas can be pressurized with a gas compressor (pneumatic pump) and stored in two accumulators. Two pressure regulators control the pressure in the vessels.

Figure 2: High pressure vessel and high pressure set-up
Calorimetric procedure of the gas hydrate formation/dissociation

The melting of pure water is used to evaluate the procedure under 1, 60 and 93 bars of methane. The sample is heated up to 20°C at 2°C/min, after a rapid cooling at –30°C to allow water crystallization (figure 3). At low pressure of methane, only one peak is detected, corresponding to ice melting. At 60 bars and higher pressures, a second peak appears after ice melting and it is moved toward higher temperature when the pressure increases. This peak is linked with the hydrate dissociation. At pressure above 80 bars, it is possible to have a good separation between the peaks corresponding to ice melting and hydrate dissociation.

![Figure 3: DSC curves of pure water under variable methane pressure](image)

Scanning mode: Methane hydrate dissociation in water

As seen in the previous experiment, the use of the temperature scanning mode is well suited to investigate the formation and dissociation of a gas hydrate. Such an experimental procedure demonstrates that the temperature of methane hydrate dissociation (onset temperature of the dissociation peak) increases with the methane pressure (figure 4). It is seen by the area under the peak that the amount of methane hydrate is proportional to the methane pressure. It is also noticed that for methane pressure above 100 bar, a small exothermic peak is detected before the endothermic dissociation effect. At this point, it is suggested that this exothermic effect is related to a recrystallization of the hydrate prior to its dissociation.

![Figure 4: DSC curves of pure water under variable methane pressure from 2 to 35 MPa (20 bar to 350 bar)](image)
The results obtained for the dissociation temperature versus methane pressure (figure 5) have been compared with data published (from Sloan E. D., *Clathrate hydrates of natural gases*, 2nd edition, Marcel Dekker, New York (USA), 1998).

**Figure 5: Methane hydrate stability curve in deionised water**

<table>
<thead>
<tr>
<th>HP micro DCS VII</th>
<th>Literature (*)</th>
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<tr>
<td>Dissociation temperature (°C)</td>
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(*) : Experimental data (E. Dendy Sloan)

(1 MPa = 10 bar)

**Isothermal mode: Methane hydrate formation in water**

In the previous experiments run in the scanning mode, the solution of water under pressure of methane is cooled down at a temperature that is sufficiently low to guarantee the formation of the gas hydrates. But this test is focused on the dissociation of the gas hydrate during the heating phase.

If the formation of the gas hydrate has to be investigated, the experimental procedure has to be adjusted as seen on figure 6 (from D. Dalmazzone, N. Hamed, C. Dalmazzone and L. Rousseau, *Journal of Thermal Analysis and Calorimetry* 85 (2006) 361-368).

**Figure 6: Curve of formation and dissociation of methane hydrate**

(\(P_{\text{CH}_4} = 30\text{MPa}\))
The solution is quickly cooled from room temperature to a given temperature and the calorimeter is stabilized at this temperature. During this isothermal level, an exothermic peak is recorded corresponding to the formation of the gas hydrate. Then by heating the solution the endothermic dissociation peak is recorded. If ΔT is the difference between room temperature and the temperature selected for the isothermal stabilization, it is seen that the shape of the exothermic peak varies with the ΔT value. It can be noticed that the hydrate formation peaks get wider and smoother as the sub-cooling degree decreases. Such an experiment also gives information on the kinetics of the formation process at a given pressure.

By directly integrating the well-defined peaks obtained with the different ΔT values, the energy released per gram of sample as a function of time is measured (Figure 8). The corresponding curves give a semiquantitative representation of the hydrate rate of formation versus. Time.

Applications to Flow Assurance

The calorimetric investigation of a sample of seawater under gas pressure (methane for example) allows the prediction of the temperature of formation and dissociation of the gas hydrate, the amount of hydrate formed (from the heat of dissociation) and the rate of formation or dissociation.

The same calorimetric test is used to investigate the different parameters that influence (and therefore prevent) the formation of the hydrate.

- Composition of the liquid medium (salt concentration, pH ...)
- Pressure according to the depth
- Action of chemical inhibitors (methanol, glycol ...)
Effect of salt on methane hydrate dissociation

The same experimental procedure is used to investigate different salt solutions under methane pressure. 14% NaCl solutions are cooled at −30°C under variable methane pressure, then heated up at 1°C/min. The methane pressure varies from 75 bar to 390 bar. The aqueous phase melting appears in two peaks (figure 9): the eutectic melting at −21°C and the progressive melting of ice in equilibrium with the saline solution around −10°C. Hydrate dissociation appears at higher temperature and the dissociation temperature increases with methane pressure.

The obtained data (dissociation temperature versus methane pressure) are compared with the model established by E. D. Sloan (from Sloan E. D., Clathrate hydrates of natural gases, 2nd edition, Marcel Dekker, New York (USA), 1998).

![Figure 9: DSC curves of 14% NaCl solution under variable methane pressure](image_url1)

![Figure 10: Methane hydrate stability curve in NaCl solution](image_url2)

There is a good experimental data for methane pressure up to 200 bar (figure 10). For higher pressure, the pre-existing model predicts dissociation temperatures that are higher than the experimental values. At 400 bar, the difference is quite significant (about 2°C). This discrepancy demonstrates that existing models cannot reproduce experimental tests.

Effect of salt and inhibitor on methane hydrate dissociation

Ethylene glycol is one of the most common inhibitors, especially during the drilling operations. In order to know what are the effects of such an inhibitor, different tests are run on a NaCl solution (100 g/l) containing an ethylene glycol solution (5.1% wt) under different methane pressures, varying from 50 bar to 390 bar.

After detecting the eutectic melting and the ice melting, the dissociation of methane hydrate is again clearly detected and the temperature of dissociation again increases with the methane pressure (figure 11).

The obtained data (dissociation temperature versus methane pressure) are compared with the Multiflash model (1), a prediction model obtained from measurements with a PVT cell. A very good fitting is observed for the full range of pressure (figure 12).
Methane hydrate formation and dissociation in crude oil emulsions with and without inhibitor

The oil and gas fields are working with complex mixtures, not water, such as crude oil emulsions. So it is important to investigate the formation and dissociation of gas hydrates in such complex fluids. A typical hydrate formation peak for a water-in-West African crude emulsion with 0.2 wt% polyvinylcaprolactam (PVCap) inhibitor is seen on figure 13 (from Jason W. Lachance, E. Dendy Sloan, Carolyn A. Koh, Chemical Engineering Science 64 (2009) 180 – 184)). The emulsion, containing the inhibitor (polyvinylcaprolactam), is cooled down to 263K and isothermally maintained at this temperature to form the hydrate.

Such an isothermal test is used to investigate the influence of the inhibitor during the formation of the gas hydrate (Figure 14). Without inhibitor, the hydrate formation occurs in a faster way together with a higher formation rate. The addition of the kinetic inhibitor is effective to delay the hydrate nucleation time.
Applications to drilling fluids

For the drilling industry, formation of gas hydrates can lead to serious operational problems and safety issues. As water depth increases with the deep offshore exploration, the potential for gas hydrate formation during the drilling operations is seriously increased. This may cause the interruption of the drilling operation due to plugging or worse the destruction of the rig equipment.

The way to prevent the problems related to the formation of gas hydrates is to add thermodynamic inhibitors to drilling fluids formulations, typically salts and glycols. The usual technique to measure the formation of gas hydrates in drilling fluids is the PVT method. But this technique does not allow the presence of solid particles in the solution. The High Pressure MicroDSC test has proved to be ideal for such determinations whatever the mud formulation (from C. Dalmazzone, B. Herzhaft, L. Rousseau, P. Le Parlouër, SPE Annual Technical Conference, Paper SPE 84315, October 2003, Denver (CO, USA)).

Two different mud formulations were tested:

- Water Based Mud (WBM) (containing NaCl 100 g/l and 2.5% glycol)
- Oil Based Mud (OBM) (containing CaCl2).

The figure 15 shows the diagram corresponding to the experiment with a water based mud. The solution is first cooled under a given pressure of methane. When heating, a first endothermic peak corresponding to the NaCl-H2O eutectic is detected, followed by the melting of the excess water. Then the peak corresponding to the dissociation of the methane hydrate is measured and the onset temperature increases with methane pressure.

Figure 15: Hydrate formation in a water based mud containing NaCl 100g/l and 2.5% glycol

Figure 16: Diagram of hydrate formation in a water based mud with different concentrations of NaCl and glycol
The obtained results allow to draw the (P,T) diagram of methane hydrate dissociation. The effect of the NaCl and glycol concentrations can be seen on figure 16. At a given pressure (i.e. a given depth), a higher concentration of glycol allows to decrease the temperature of hydrate dissociation. With the addition of NaCl, the decrease is enlarged. The same study can be run with oil based mud (figure 17).

From the corresponding data, if the temperature and pressure profiles are known for a given drilling operation, it will possible to predict the risk for hydrate formation if there is a circulation stop the drilling mud as this will induce a temperature decrease (figure 18).

![Figure 17: Hydrate formation in a oil based mud containing CaCl₂ and emulsifier](image)

![Figure 18: Prediction of risk for formation of gas hydrates](image)

**Environmental applications: CO₂ storage**

Carbon capture and sequestration (CCS) technologies play a critical part in the attempts to reduce the atmospheric carbon dioxide content. Common CO₂ sequestration techniques involve direct injection into geologic formations such as depleted oil or gas reservoirs, or deep unminable coal seams. An alternative approach is the injection of CO₂ into natural methane hydrate deposits in ocean sediments. In this case, formation of carbon dioxide hydrates is expected, together with a dissociation of methane hydrates.

Calorimetry has proved to be a valuable technique in the investigation of gas hydrate formation and dissociation [see previous examples]. The technique is used to investigate the formation and dissociation of CO₂ hydrates to measure the corresponding temperatures and enthalpies of reaction.

For such an investigation, a multi-cycle mode (successive cooling and heating) of formation of hydrate is applied in order to accelerate the process (D. Dalmazzone and al, Chemical Engineering and Processing 45 (2006) 184–192). THF is also added to the solution to enhance the formation of CO₂ hydrate. Heating and cooling cycles between -15°C and 5°C are run at 1°C.min⁻¹ on a 37.55mg on a THF solution. A constant CO₂ pressure of 20 bar is applied.

After 5 cycles (figure 19), the heating curve distinctly shows the melting of free water followed by the endothermic peaks corresponding to the formation of the CO₂/THF co-hydrate and the CO₂ hydrate.
A deconvolution software allows to make a clear distinction between the different effects. The heat of melting of the CO\textsubscript{2} hydrate is equal to 12.18 J.g\textsuperscript{-1} of solution, i.e. 13.56 J.g\textsuperscript{-1} of water. The comparison with literature value of the heat of dissociation of CO\textsubscript{2} hydrate (\(\Delta H_{\text{diss}} = 500,11\) J.g\textsuperscript{-1} H\textsubscript{2}O) allows determining a ratio of hydrate formation of 2.7%.

After 28 cycles, the free water has completely disappeared and a sharper and larger endothermic effect, indicating that a larger amount of hydrates is produced (figure 20). If the same test is only run with deionized water under the same experimental conditions, the curve (figure 21) shows that the CO2 hydrate formation occurs at a lower temperature. The comparison clearly indicates the stabilizing effect due the presence of THF in the hydrate structure (peak temperature shift of 7.7°C).

Despite the absence of water melting peak, hydrates of pure water and THF melting peaks respectively correspond to similar amounts of 6.93% and 6.92% only. The HPMicroDSC was also used to investigate the isothermal formation of CO\textsubscript{2} hydrate at 2°C in a 10% THF solution under 30 bar of CO\textsubscript{2}. The solution is cooled from 25°C to 2°C at 1°C.min\textsuperscript{-1} and isothermally maintained at 2°C during several hours. After 1 hour 35 minutes, the exothermic peak that characterizes the hydrate formation is clearly detected. This time is equivalent to the induction time of hydrate formation.