

THERMODYNAMIC STUDY OF UNDERSATURATED HYDRATES FORMED FROM A GAS MIXTURE IN MARINE SEDIMENTS

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1. INTRODUCTION

Gas hydrates are crystalline compounds which can be formed when water or ice and suitably sized molecules are brought together under favorable conditions. Small sized molecules, such as the natural gas ones fit suitably in the hydrate lattice producing solid phase, which despite its resemblance to common ice, it contains substantial amounts of natural gas (1 m³ of gas hydrate can produce up to 175 Nm³ of natural gas). The pressure-temperature conditions for their formation depend mainly on the composition of the gas and of the water-rich phase. Conditions favorable for gas hydrate formation can be found in permafrost regions and mainly in marine environments. Over 95% of the estimated gas hydrates globally are considered to be found below the seabed.

While both single and multi component natural gas can be enclathrated in the hydrate phase in natural environments, the up-to-present research focuses primarily on single-gas-component hydrates. This may be appended both to the higher complexity of the thermodynamic behavior of the multi-component hydrates, as well as to the fact that the most hydrates discovered so far were found either on the surface or at a depth of a few meters and were comprised of almost pure methane.

The conducted research is part of a wider project targeted to evaluate the environmental conditions of the “Anaximander” mud volcanoes’ seabed, an area of the East Mediterranean sea where gas hydrates were found from previous exploration cruises. The aim of this study is to assess the thermodynamic behavior of a ternary gas (C₁ to C₃) of thermogenic origin at conditions well inside the hydrate formation region (13 to 20 Mpa pressure and 12 to 20 °C temperature). The fractionation of the enclathrated gas components has been experimentally observed and measured at these conditions and at different salinity levels.

The results reveal that in hydrate undersaturated conditions such as the ones found in the “Anaximander” area, gas hydrates can be formed mainly from gas components dissolved in the pore water, even in the absence of any free gas phase. Moreover, the fractionation of gas components in the hydrate phase with respect to temperature should lead to a compositional variation with depth of the gas contained in the GH below seabed.

2. MATERIALS AND METHODS

The experimental setup that was used for the phase behaviour study is presented schematically in Figure 1.

A syringe pump is connected to two piston cylinders, one containing de-ionized water and the other containing the gas mixture of the study. Gas is injected to the reactor, which is equipped with magnetic stirrer. The reactor is in a refrigerated bath, which controls the temperature. The temperature of the reactor and the cooling bath is monitored by a temperature measuring device equipped with digital output (accuracy 0.03 °C). The pressure of the reactor and the water cylinder is measured through pressure transducers with an accuracy of 0.01Mpa and the analog signals are routed through a data acquisition card to a PC (not displayed in Figure 1). The digital outputs from the temperature device and the pump (pump volume, flow rate, and pressure) are also routed to the same PC, where they are logged and displayed by a specially designed software program. Composition measurements of the dissolved gas were performed with a gas chromatograph.

Naturally occurring hydrates are homogeneous due to the constant prevailing conditions over a geological timescale. Nevertheless in the lab heterogeneous hydrates are produced due to the selective enclathration of the gas components in the hydrate phase in the short experimental timescale. Heavier hydrocarbons tend to form hydrates first, leaving the lighter components, such as methane, to the outer boundary of the hydrate agglomerate. In order to study the gas mixtures at conditions inside the hydrate stability limits, it was necessary at first to develop a procedure to produce homogeneous gas hydrates in the laboratory. Once the procedure was defined and verified a series of measurements was conducted to study the thermodynamic behaviour of the hydrate – water system at each set of selected pressure-temperature conditions. After thermodynamic equilibrium was achieved for each set of conditions, the amount and composition of the gas dissolved in the water were measured. The gas composition of the hydrate phase was assumed to be practically identical to the initial gas composition, an assumption based both on the small quantity of liquid water that remains in equilibria with the hydrate in the reactor (≈ 75 ml), and on the low solubility of gas in the water phase at these conditions.

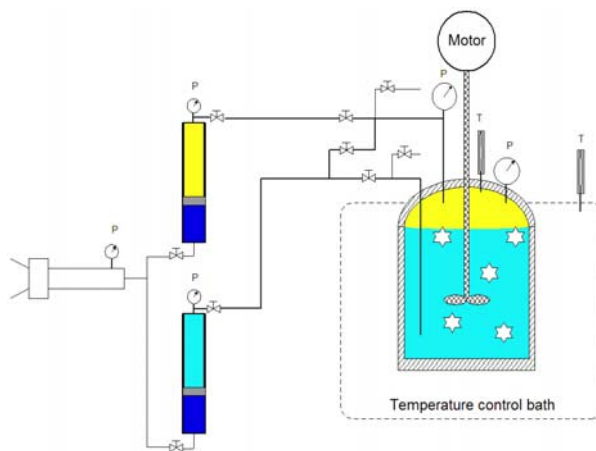


Figure 1: Experimental setup used for gas hydrate phase behaviour tests.

3. RESULTS - CONCLUSIONS

The results are presented in Figure 2 in the form of concentration of the gas components (mole fractions of C_1 to C_3) in the water phase.

The conclusions derived from this series of measurements are the following:

1. Solubility of the gas components increases with temperature. The results reveal that gas hydrate formation is possible in a natural environment, such as the "Anaximander" seabed one, even if the free gas phase is not present. The cooling of liquid fluxes as they rise through the subsea sediments causes the formation of gas hydrates from dissolved gas. The composition of the hydrates depends on the change of solubility of the gas components with respect to temperature.
2. Since C_1 solubility decreases more sharply with temperature than the C_2 and C_3 ones, almost pure-methane hydrates are expected to be formed due to the aforementioned cooling at shallower sediment zones close to seabed. This conclusion may explain the recovery of almost pure methane hydrate at sediments near the seabed during exploration cruises.
3. Gas solubility decreases as pressure increases. The dissolved gas tends to form hydrates as pressure increases, in contrast to what is observed in a V-Lw equilibria, where gas solubility increases with pressure. Pressure reduction at constant temperature results in the mass transfer of gas components from the hydrate phase into the liquid water phase. Since this mass transfer is selective among the enclathrated gas components, a reduction in pressure will change the dissolved gas composition towards the heavier components.

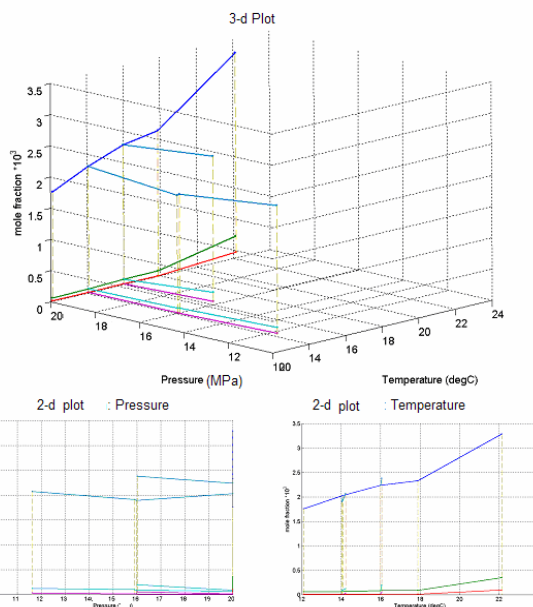


Figure 2: Equilibria data for the dissolved gas at Lw-I conditions.

blue line = C_1 green line = C_2 red line = C_3

4. ACKNOWLEDGEMENTS

The European Community – Research Directorate, for financing the “Anaximander” project.