**EXPERIMENTAL AND MODELING STUDIES ON THE H2O-CH4-NH3 SYSTEM WITH APPLICATION TO TITAN.** E. Gloesener¹, M. Choukroun², T. H. Vu¹, A. G. Davies¹, A. Desmedt² and C. Sotin¹, ¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States (elodie.d.gloesener@jpl.nasa.gov), ²Institut des Sciences Moléculaires, Talence, France, ¹Nantes Université, Laboratoire de Planétologie et Géosciences, Nantes, France.

**Introduction:** Clathrate hydrates have long been inferred to constitute methane reservoirs within the icy shell of Titan [1-2]. Their dissociation and subsequent methane outgassing could be enhanced by interactions with ammonia [2], an important thermodynamic inhibitor and a likely source of Titan’s atmospheric nitrogen [3]. Although advances continue to be made in our understanding of the outgassing processes on Titan, experimental equilibrium data are still lacking to comprehensively interpret the effects of ammonia on clathrate hydrates and their destabilization.

In this work, we present the results of laboratory and modeling studies that evaluate the role of ammonia on the stability of clathrate hydrates and implications for the replenishment of Titan’s atmospheric methane.

**Methods:** Experimental setup: The dissociation temperature of methane clathrate hydrates was measured by a high-pressure microcalorimeter (µ-DSC7 evo Setaram) that allows operation from 228.15 K to 393.15 K. Pressure was controlled via a piston compressor connected to the microcalorimeter enabling experiments up to 400 bars of methane. The high-pressure cells, designed to contain up to 0.5 ml of sample, were placed inside the two block cavities of the furnace. The reference cell remained empty and pressurized during the whole run, while the measurement cell was filled with ~60 μL of H2O-NH3 solution (5-10 wt% NH3). To ensure the complete conversion of water ice into clathrate hydrates, we adopted a multicycle procedure where the sample was cooled at 1 K/min to 243.15 K and then heated at a temperature sufficient to melt the remaining ice but cold enough to avoid clathrate dissociation. Each cooling-heating cycle was repeated 30 times before performing a heat ramp from 243.15 K to 300.15 K at 0.1 K/min. The run was pre-programmed and monitored through the Calisto software (Setaram).

**Thermodynamic model:** We developed a novel approach based on the standard method of van der Waals and Platteeuw [4] where clathrate dissociation pressures are simulated considering the effect of ammonia on the behaviour of water. For that purpose, we expressed the activity coefficient of water in the liquid phase γ_H2O based on the Margules equation as proposed by Choukroun and Grasset [5]:

\[ RT \ln(\gamma_{H2O}) = W(1 - X_{H2O})^2 \]

where \( R \) is the ideal gas constant, \( T \) is the temperature and \( X_{H2O} \) is the molar fraction of H2O. The Margules coefficient \( W \) is adjusted as a function of temperature and pressure such as:

\[ W = w_0(1 + w_1 \tanh(w_2P))(1 + w_3T + w_4/T) \]

where \( w_0, w_1, w_2, w_3 \) and \( w_4 \) are constant parameters.

**Preliminary results:** The thermogram of methane clathrate hydrates obtained at 100 bars with 5 wt% NH3 ammonia in the system is shown in Figure 1. Dissociation occurs at 284.9 K (peak temperature). This temperature is colder than the 286 K dissociation peak of methane clathrates without ammonia in the system, and is in agreement with previous Raman spectroscopy studies [6]. In the presence of ammonia, the broader shape of the endothermic peak indicates a partial dissociation behavior similarly to what was observed for tetrahydrofuran (THF) clathrate hydrates [7].

![Figure 1: Heating thermogram of methane clathrate hydrates obtained by the multicycle method at 100 bars and 0.1 K/min.](image)

Our new thermodynamic model reproduces the decrease of the dissociation temperature of methane clathrates with ammonia concentration in agreement with experimental data (Figure 2). Future work involves the acquisition of additional calorimetry data and the update of the Margules coefficients from methane clathrate data.
Implications for Titan: Methane outgassing on Titan may occur without requiring extensive cryovolcanic eruptions. The presence of small amounts of ammonia in the subsurface could potentially trigger partial dissociation of methane clathrates on warming and lead to a gentle (non-explosive), gradual release of methane at the surface.

Figure 2: Dissociation temperature of methane clathrate hydrate in the presence of ammonia simulated with our model and comparison with experimental data at 50 and 100 bars [6].

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