EXPERIMENTAL STUDY OF THE EFFECTS OF FREEZING ON LIQUID HYDROCARBONS ON THE SURFACE OF TITAN. K. Farnsworth[1], Z. McMahon[1], D. Laxton[1], V. Chevrier[1], J. M. Soderblom[2]. [1]University of Arkansas, Center for Space and Planetary Sciences FELD 202, University of Arkansas, Fayetteville, AR 72701. (kkfarnsw@email.uark.edu). [2]Massachusetts Institute of Technology, Department of Earth, Atmospheric and Planetary Sciences, 77 Massachusetts Ave, Cambridge, MA 02139.

Introduction: Titan is the only body in the Solar System, besides Earth, with a dense nitrogen atmosphere and stable surface liquids. Titan's atmosphere is predominantly nitrogen, with several percent methane, which enables a methane hydrologic cycle [1]. Ethane also participates in this cycle and is generated via methane photolysis [2]. This atmosphere creates an environment in which lakes of methane and ethane are stable on Titan's surface [2]. The surface temperature at Titan's poles falls to ~91 K [3], close to the freezing temperature of ethane. This means that ethane ice may be stable for short periods in time on Titan in local regions where temperatures locally drop below the mean regional temperature (e.g., if a pond evaporative cools).

In this preliminary analysis, experimental data acquired from freezing ethane and methane-ethane mixtures in a nitrogen atmosphere, are presented. This study focuses on the freezing process of ethane, as well as the dynamics of methane-ethane mixtures involving the dissolution of nitrogen. We explore the relationship between liquid methane, liquid ethane, nitrogen gas, and temperature. Our work helps to better understand the thermodynamic processes that may occur in Titan's surface liquids.

Methods: Experiments were conducted in the University of Arkansas' Titan surface simulation chamber [4]. This chamber maintains a temperature of ~94 K and a pressure of 1.5 bar using liquid and gaseous nitrogen, respectively. The sample is condensed to liquid phase directly from a gaseous phase and is delivered into a petri dish connected to a hanging electronic balance. Once the liquid has accumulated in the petri dish, the temperature is lowered to ~87 K to induce freezing. Mass and temperature are continuously recorded for the duration of the experiment.

Results/Discussion: As a preliminary study, we investigate the freezing points of pure methane and pure ethane in a 1.5 bar nitrogen atmosphere. Figures 1–3 present example elements of these experiments. These include temperature data (Fig. 1), images of the sample (Fig. 2) and spectra of the sample (Fig. 3).

We find that, in a 1.5-bar nitrogen atmosphere, the freezing temperature of ethane has an average freezing point of 87.59 K (with error). Methane, however, remains liquid down to at least 86 K. Nitrogen dissolution suppresses the freezing temperatures of these liquids. Nitrogen, however, is considerably more soluble in methane than ethane [5, 6, 7] and, therefore has a much greater effect on the freezing temperature of methane. Our results suggest that ethane, but not methane, may be able to freeze on Titan.

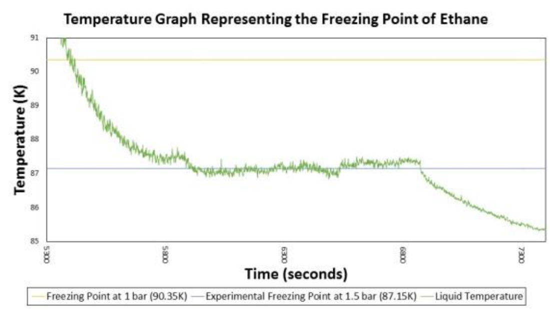

Figure 1: Temperature graph representing 87.15 K as the freezing point of ethane at 1.5 bar.

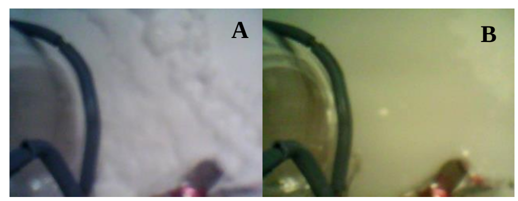

Figure 2: Images of ethane in a frozen state (**A**) and liquid state (**B**).

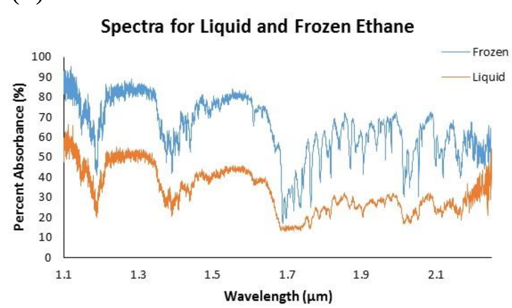

Figure 3: Spectra representing frozen and liquid ethane. The shift in percent absorbance indicates freezing has occurred.

Next we investigate the freezing temperature and nitrogen solubility/dissolution (often in the form of nitrogen bubbles) of methane-ethane mixtures. Following the same procedure and using varying concentrations of methane and ethane, we lowered the temperature to 87 K (the lowest temperature we consider reasonable for Titan) to determine if any ices form. After about 30 minutes, the temperature was raised to 104 K to determine the melting temperate of any ices that accumulated and to study the effects of nitrogen dissolution. An ice layer is observed to form at the edge of the petri dish when the ethane concentration is greater than 20%. As the sample is initially warmed, bubbles are observed (Fig. 4), often becoming trapped beneath any ice layer that may have formed. Once the temperature has increased further, the ice melts and the bubbles are able to reach the surface. Based on the boiling points of methane, ethane, and nitrogen at 1.5 bar (125 K, 90 K, and 83 K, respectively), these bubbles are most likely nitrogen. We believe that as the sample is cooled, some amount of ethane is separating from the methane-nitrogen-ethane mixture and is freezing. The remaining methane-rich liquid can then absorb additional nitrogen (since nitrogen is more soluble in methane than ethane [7]). As the sample is warmed, the solubility of nitrogen decreases for two reasons: the increase in temperature and the increase in the ethane concentration as the ice melts [6]. This results in nitrogen dissolution. This model is described in greater detail in Fig. 5. Nitrogen was not directly detected, nor is it possible to analyze the bubble contents at this time, but nitrogen is extremely likely to have caused this phenomenon.

The amount of degassing observed depends on methane concentration. There is a shifted bell curve with a peak around 70 mole% methane and no bubbles being formed at both 100% methane and 100% ethane concentrations (Fig. 6). This is consistent with the theory that the variation of the methane-ethane concentration during the temperature cycle is significant. Also observed during bubble formation were temperature drops of up to 10 K in ~10 seconds (Fig. 7). This significant decrease in temperature indicates substantial amounts of energy being removed from the liquid by this degassing process.

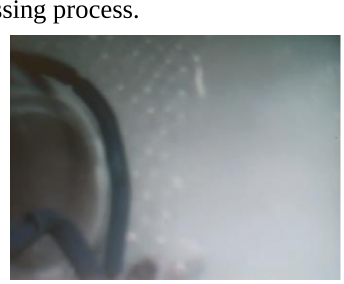

Figure 4: An image from above of nitrogen bubbles covering half the petri-dish.

Summary: We find that changes in ethane / methane concentration could result in nitrogen degassing in Titan's lakes. We propose that the freezing/melting of ethane results in changes in the methane-ethane concentration that can influence nitrogen solubility, resulting in the dissolution / exsolution of nitrogen gas. This should have significant implications for Titan lakes and rain. Additional experiments will be conducted to improve accuracy of the freezing point of ethane in a 1.5-bar nitrogen atmosphere, and to determine the homogeneity of the mixture, as well as to either accept or refute the ethane ice hypothesis.

Liquid Evolution Model

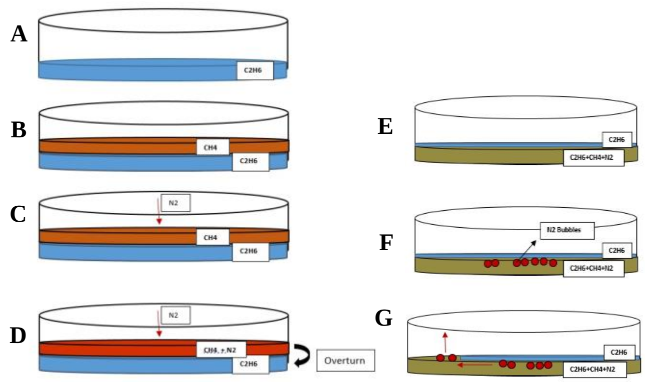

Figure 5: Liquid evolution model. A hypothesis of bubble formation.

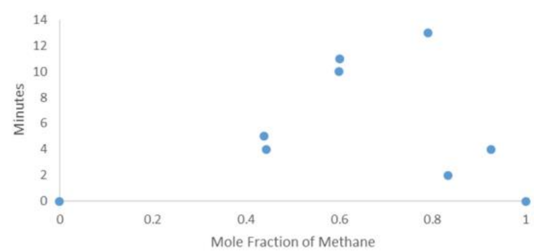

Figure 6: Represents methane mole fraction effect on bubble duration.

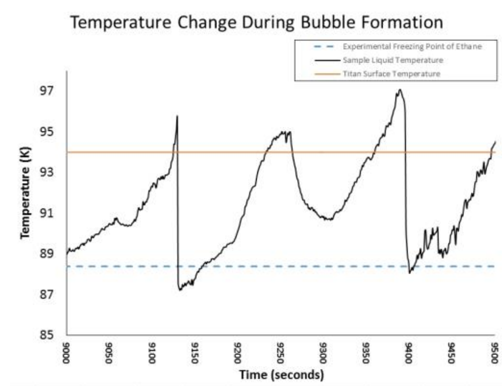

Figure 7: Temperature dips during bubble formation.

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References: [1] Lunine J.. and Atreya S. K. (2008) *Nature Geosci., 1,* 335. [2] Wilson E. H. and Atreya S. K. (2004) *JGR 109:*E06002 [3] Jennings D. E. (2011) *Ap. J. 737*, L15. [4] Wasiak F. C. et al. (2013) *ASR 51*, 1213-1220 [5] Luspay-Kuti A. et al. (2012) *GRL 39*, L23203. [6] Luspay-Kuti A. et al. (2014) *EPSL 410,* 75-83 [7] Battino R. et al. (1984) *J. Phys. Chem. Ref. Data 13,* 563.