EXPERIMENTAL STUDY OF NITROGEN DISSOLUTION IN METHANE-ETHANE MIXTURES UNDER TITAN SURFACE CONDITIONS.

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Introduction: Besides Earth, Titan is the only known planetary body with a dense nitrogen-dominated atmosphere, and stable liquids on its surface. Titan's atmosphere contains several percent methane, which drives a methane hydrologic cycle [1] and includes small amounts of ethane, produced via methane photolysis [2]. Methane, along with small amounts of ethane, collect on the surface forming stable lakes [2]. The exact concentration of methane and ethane in these lakes is under debate [3,4]. For example, Brown et al [3] suggests that ethane is the dominate hydrocarbon in Ontario Lacus, while Mitchell et al suggest methane is the dominate component of Ligeia Mare [4].

The lack of experimental data of methane-ethane-nitrogen mixtures at Titan surface temperatures and pressures, result in uncertainty in thermodynamic and kinetic parameters [5], which hinder lake composition models. This study aims to determine the solubility of nitrogen in liquid hydrocarbons under Titan surface conditions. These results are important for thermodynamic modeling and to improve the understanding of evaporation and freezing of Titan's hydrocarbon lakes.

Methods: The experiments were conducted at the University of Arkansas in a Titan surface simulation chamber [6]. This chamber maintains a temperature of ~94K and a pressure of 1.5 bar using liquid nitrogen and nitrogen gas, respectively. The sample is condensed to liquid phase directly from a gaseous phase and is delivered to a petri dish connected to a hanging electronic balance. Mass and temperature are recorded for the duration of the experiment. This data is used to determine the evaporation rate, sample concentrations, and nitrogen mole fraction.

In this analysis, data obtained for pure methane [5] and methane/ethane mixtures in a nitrogen atmosphere [7] are used. Nitrogen dissolution is expected in the "plateau section" [7] of the mass curve (Fig. 1), thus the focus of this study. The duration of the "plateau", created by the mass balance between methane evaporation and nitrogen dissolution, is used to estimate the amount of dissolved nitrogen. It is assumed that methane evaporates at the same rate throughout the experiment. We assume that the amount of nitrogen dissolution that occurs as methane is poured into the petri dish is small. Evaporation rates of methane and methane-ethane mixtures are then determined from a least-square fit to the steady-state portion of the mass vs. time curves [5, 7] and the deviation from this initial evaporation rate (the plateau region) gives the theoretical weight of dissolved nitrogen. This weight is then converted to a mole fraction.
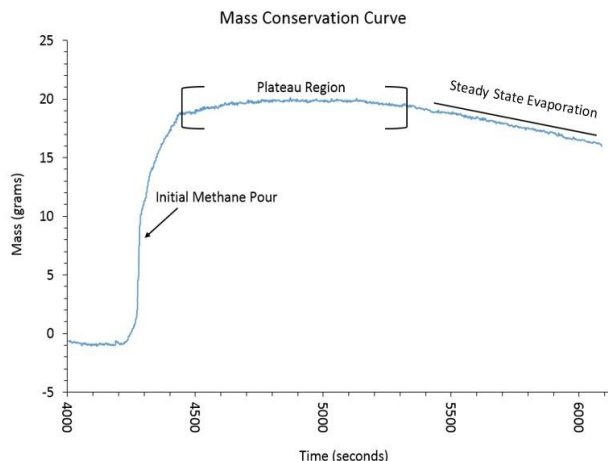

Figure 1: Experimental data for pure methane represented in a mass conservation curve. This mass versus time graph shows the plateau zone after a methane pour, from ~4400 to 5300 seconds, followed by the steady-state evaporation.

Results/Discussion: The preliminary data regarding the dissolution of nitrogen in pure methane and methane-ethane mixtures, are shown in Figures 2 and 3. We explore the solubility of nitrogen as a function of methane concentration in methane-ethane mixtures and of temperature in pure methane. We find that the fraction of dissolved nitrogen exponentially increases with a linear increase in methane concentration (Fig. 2), and that nitrogen solubility in pure methane is inversely related to temperature (Fig. 3). While there is some uncertainty in the slope of the exponential trend, the relationship between methane fraction, temperature, and fraction of dissolved nitrogen is clear.

The dissolution of nitrogen in methane-ethane mixtures increases from a 1 mol% of nitrogen at 74 mol% methane, to ~ 20% nitrogen in 100% methane. There is no observable nitrogen dissolution in the experimental data for pure ethane liquid [7], hence, we assume it is negligible compared to the role of methane during the time period of our experiment. This study confirms that nitrogen dissolves far more easily in methane than in ethane [8].

In regards to pure methane, the large spread of nitrogen mole percent values correlates with the temperature of the sample liquid. In Figure 2, the red circles correspond to temperatures between 92 K and 95 K, which are closest to Titan surface temperatures of 91–94 K. The blue circles correspond to cooler temperatures below 92 K and the green circles are warmer, above 95K. The black points are not considered in this section of the discussion, because the temperature of the liquid was not available [7]. The amount of dissolved nitrogen varies by approximately a factor of 4 between the coolest and warmest temperatures considered. The average nitrogen mole fraction of the coldest temperature (below 92K), middle temperature (between 92 K and 95 K), and the warmest temperatures (above 95K) are 0.318, 0.159, and 0.072, respectively. Within this temperature range, nitrogen dissolution decreases by a factor of ~ 2/3 per degree K, implying a strong dependence of nitrogen dissolution on the temperature. Thus, a small change in Titan's surface temperature can strongly influence the concentration of dissolved nitrogen in Titan's lakes.

Malaska et al. [9] report similar exponential trends with mole fraction of nitrogen in methane/ethane mixtures (Fig. 2) and methane with temperature (Fig. 3). However, their study shows a smaller slope in exponential trend, with a much greater mole fraction of nitrogen at lower concentrations of methane. This discrepancy is likely due to the difference in experimental protocol. Malaska et al. derive their data from the change in pressure of a closed system with a small atmosphere, while our experiments are in an open system with a large atmosphere, and we derive its data from the change in mass. Also, unlike this study, Malaska et al. do not consider methane evaporation.

Even though an open system is a better analog to Titan's surface, we are unable to distinguish mass from methane verses nitrogen in the first five minutes of dissolution. This is due to the lag time in liquid transfer from the condenser to the petri dish. Thus, if the majority of nitrogen dissolution is occurring in the first five minutes then we are unable to detect it. This may be the main cause of the difference between our results and those of Malaska et al. between 0–0.8 mole fraction of methane in Figure 1.

Conclusion: The results of this study demonstrate that nitrogen is much more soluble in methane than ethane and the amount of nitrogen able to dissolve in methane and methane-ethane mixtures is highly dependent on temperature. This suggests small changes to Titan's surface temperature will have a dramatic effect on nitrogen dissolution. Further analysis will enable more accurate nitrogen dissolution estimates involving methane-ethane mixtures at Titan surface conditions.
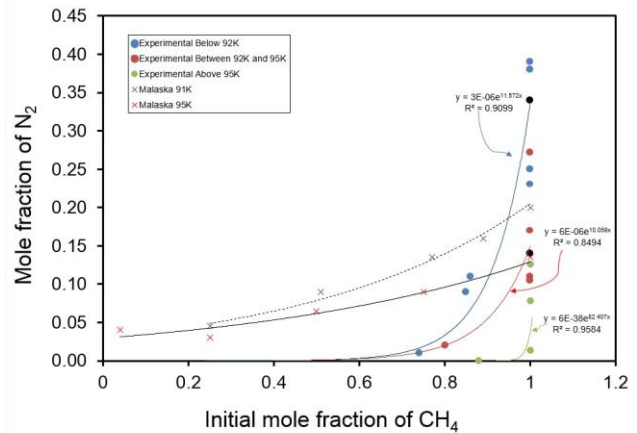

Figure 2. Mole fraction of dissolved nitrogen as a function of the initial mole fraction of methane in a methane/ethane mixture. An exponential increase of nitrogen solubility is observed with increasing methane above 0.7 mole fraction of methane, and a decreasing mole fraction with increasing temperature in pure methane. These findings are compared to Malaska et al. [9].
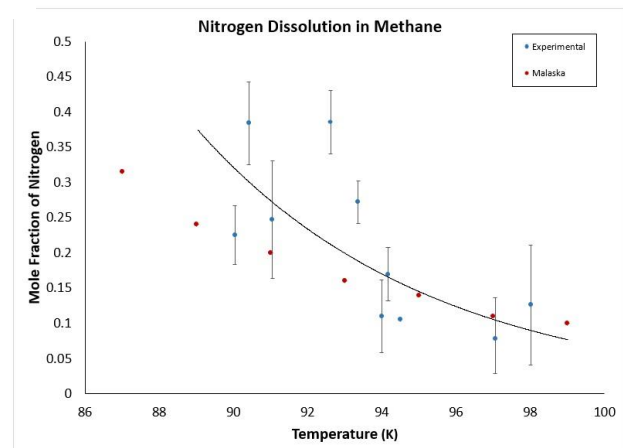

Figure 3. The change in nitrogen dissolution in 100% methane in regards to increasing temperature. These findings are compared to Malaska et al. [9].

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] Brown et al. (2008) *Nature 454*, 607-610. [4] Mitchell et al. (2015) *GRL 42*, 1340-1345. [5] Luspay-Kuti A. et al. (2012) *GRL 39*, L23203. [6] Wasiak F. C. et al. (2013) *ASR 51*, 1213-1220. [7] Luspay-Kuti A. et al. (2014) *EPSL 410,* 75-83. [8] Battino R. et al. (1984) *J. Phys. Chem. Ref. Data 13,* 563. [9] Malaska et al. (2016) *LPSC 47,* Abstract #1729.