

EXPERIMENTAL INVESTIGATION OF LIQUID HYDROCARBONS ON THE SURFACE OF TITAN: NITROGEN DISSOLUTION, EXSOLUTION, AND KINETICS. K. Farnsworth¹, Z. McMahon¹, D. Laxton¹, S. Singh², A. Luspai-Kuti³, J. M. Soderblom⁴, V. Chevrier¹. ¹University of Arkansas, Center for Space and Planetary Sciences FELD 202, University of Arkansas, Fayetteville, AR 72701. (kkfarnsw@email.uark.edu). ²Bear Fight Institute, 22 Fiddler's Rd, Winthrop, WA 98862. ³Southwest Research Institute, 6220 Culebra Rd, San Antonio, TX 78238. ⁴Massachusetts Institute of Technology, Department of Earth, Atmospheric and Planetary Sciences, 77 Massachusetts Ave, Cambridge, MA 02139-4307.

Introduction: Besides Earth, Titan is the only known planetary body with a thick nitrogen (N_2) atmosphere, and stable liquids on its surface. Titan's N_2 atmosphere and smaller atmospheric constituent, methane (CH_4), allows the moon to have a methane hydrologic cycle [1] and the minor presence of ethane (C_2H_6), through methane photolysis [2]. These processes create stable CH_4 - C_2H_6 dominated lakes on Titan's surface [2]. These lakes are possible due to the triple point (~ 91 K) of CH_4 and C_2H_6 falling very close to Titan temperatures. This means C_2H_6 and CH_4 ice could also be a strong possibility if Titan becomes slightly colder or if specific processes allow temporary cooling of the surface.

In this study, experimental results in the CH_4 - C_2H_6 - N_2 ternary system are presented. We focus on processes such as dissolution and exsolution as a function of temperature, as well as kinetics of N_2 gas into varying CH_4 - C_2H_6 liquid mixtures. The outcome of this study will improve our understanding of geological processes occurring on Titan's surface.

Methods: The experiments were conducted at the University of Arkansas' Titan surface simulation chamber [3] which retains a temperature of ~ 94 K and pressure of 1.5 bar N_2 using liquid N_2 and N_2 gas, respectively. The sample is condensed from gas to liquid phase inside a condenser, then released onto a petri dish connected to a hanging electronic balance. Here, the temperature is either kept steady in the case of N_2 dissolution and kinetics or lowered to ~ 85 K then warmed for exsolution. Mass and temperature are continuously recorded for the duration of the experiment.

Results/Discussion: Nitrogen Dissolution.

Here we explore the solubility of N_2 as a function of CH_4 concentration in CH_4 - C_2H_6 mixtures (Fig. 1) and temperature in pure CH_4 (Fig. 2). We find dissolved N_2 exponentially increases with a linear increase in CH_4 concentration, and N_2 solubility in pure CH_4 is inversely related to temperature.

The dissolution of N_2 in CH_4 - C_2H_6 mixtures increases from a 1 mol% of N_2 at 74 mol% CH_4 , to $\sim 15\%$ N_2 in 100% CH_4 . Since N_2 does not show noticeable dissolution in C_2H_6 [4], we assume it is

negligible compared to the role of CH_4 during our < 1 hour of dissolution. This study confirms that N_2 dissolves far more easily in CH_4 than in C_2H_6 [5].

With 100% CH_4 , the large spread of N_2 mole fraction values correlates to the temperature of the sample liquid. We see an exponential trend with a change of ~ 10 mole% CH_4 change per $\sim 1^\circ$ K, implying a strong dependence of N_2 dissolution on temperature. Thus, a small change in Titan's surface temperature can strongly influence the concentration of dissolved N_2 in Titan's lakes.

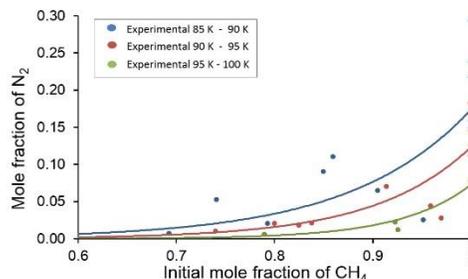


Figure 1. Mole fraction of dissolved N_2 as a function of initial mole fraction of CH_4 in a CH_4 - C_2H_6 mixture. An exponential increase of N_2 solubility is observed with increasing CH_4 above 0.7 mole fraction of CH_4 , and a decreasing mole fraction with increasing temperature in pure CH_4 .

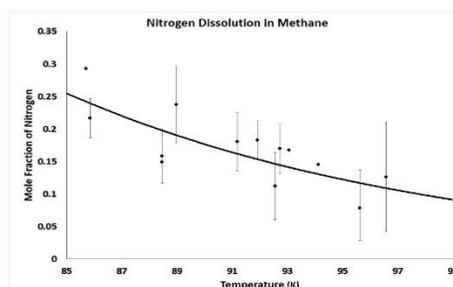


Figure 2. An exponential trend with N_2 dissolution in 100% CH_4 with decreasing temperature.

Nitrogen Exsolution: Since N_2 dissolution occurs in CH_4 , N_2 exsolution also occurs, occasionally in the form of bubbles. For exsolution experiments, varying concentrations of CH_4 and C_2H_6 were lowered to ~ 85 K to induce freezing of C_2H_6 and then raised to ~ 102 K. During this warming transition, bubbles began

forming rapidly where the mixture visually appeared to be in a liquid state (Fig. 3), and in another area larger bubbles moved under an ice layer. These bubbles are 0.83 – 5.5 mm in diameter.

Additionally, the interaction of CH₄, C₂H₆, and temperature drive the formation of N₂ bubbles. The liquid evolution model (Fig. 4) describes this hypothesis in greater detail. The duration of the bubble release follows a Gaussian-shaped curve with varying CH₄-C₂H₆ concentration with a peak around 67 mol% CH₄. Subsequently, 100% CH₄ and 100% C₂H₆ result in a lack of surface bubble formation (Fig. 5). Also, bubbles have associated temperature dips. The most significant recorded was ~10 degrees Kelvin in 12 seconds resulting from the largest concentration of bubble formation. This significant decrease in temperature indicates an endothermic reaction with a positive enthalpy. Therefore, the solution is not ideal.



Figure 3: An image from above of N₂ bubbles covering half the petri-dish.

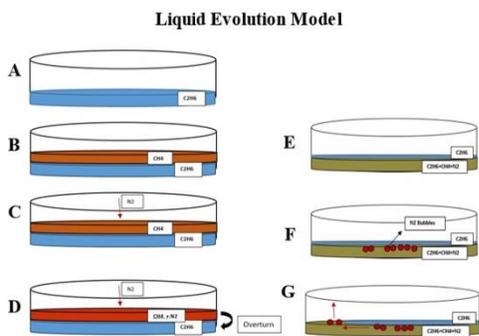


Figure 4: Liquid evolution model. A hypothesis of N₂ bubble formation.

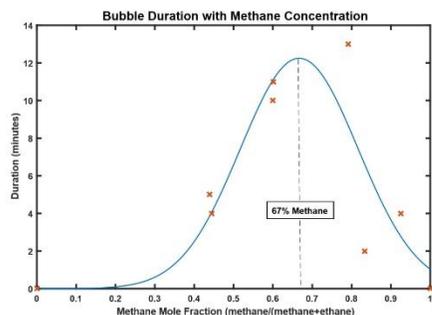


Figure 5: Bubble duration versus CH₄ mole fraction.

Kinetics: This section introduces the next steps in our hydrocarbon experiments: the kinetics and rate of dissolution of N₂ gas in liquid CH₄. The formation of bubbles is a dynamic process and understanding the kinetics of N₂ dissolution is of prime importance for explaining these observations. This study utilizes the plateau and steady state evaporation sections of the mass vs. time curve to understand the dissolution and diffusion processes as N₂ crosses the gas-liquid interface. After setting the beginning of dissolution to zero and correcting for CH₄ evaporation (Fig. 6), the rate of N₂ saturation can be calculated through modeling. These rates will further our understanding of CH₄-N₂ mixtures in Titan’s lakes and contribute to Titan lake and surface-atmosphere interaction models.

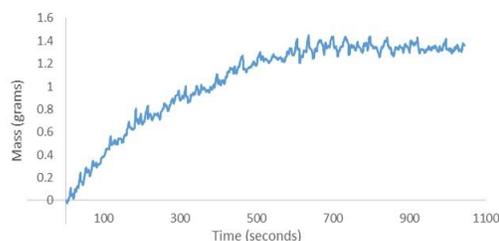


Figure 6: An example of a slope corrected mass vs. time curve. This mixture has an original composition of 97% CH₄ and 3% C₂H₆ at 93.6 K. N₂ comprises 1.3 g or 1.8%, and reached saturation in ~600 seconds.

Conclusion: This study investigates how varying CH₄-C₂H₆ mixtures interact with a 1.5 bar N₂ atmosphere. We conclude N₂ dissolves into CH₄ more readily than C₂H₆. Above 70% CH₄, we see an exponential trend with increasing CH₄ percentage and an exponential trend with decreasing temperature in 100% CH₄ is also present. Furthermore, N₂ bubbles have the highest bubble population at ~67 mol% CH₄. Now we are beginning to explore kinetics and rate of dissolution of N₂ gas in liquid CH₄. The results of this study are important in improving Titan thermodynamic and atmospheric models, as well as to advance our understanding of geologic and kinetic processes on Titan’s surface and lakes.

Acknowledgements: This work was funded by NASA Outer Planets Research Program #NNX10AE10G and the NASA Cassini Data Analysis Grant #NNX15AL48G.

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] Wasiak F. C. et al. (2013) *ASR*, 51, 1213-1220 [4] Luspay-Kuti A. et al. (2014) *EPSL*, 410, 75-83 [5] Battino R. et al. (1984) *J. Phys. Chem. Ref. Data*, 13, 563.