

EXPERIMENTAL STUDY OF NITROGEN DISSOLUTION IN METHANE-ETHANE MIXTURES UNDER TITAN SURFACE CONDITIONS. V.F. Chevrier¹, A. Luspay-Kuti¹, S. Singh¹. ¹University of Arkansas, Center for Space and Planetary Sciences (FELD 202, University of Arkansas, Fayetteville, AR 72701.(vchevrie@uark.edu).

Introduction: Titan is the only other known planetary body besides the Earth with stable liquids on its surface. In addition, it possesses a massive N₂ atmosphere with CH₄ as the second most abundant constituent. Methane displays a meteorological cycle in Titan's troposphere [1], and is thought to be a major compound in the surface liquid reservoirs. The principal product of methane photolysis in Titan's stratosphere and ionosphere is ethane, which condenses and accumulates on the surface, forming bodies of liquid according to photochemical models [2].

Titan's dense nitrogen atmosphere and hydrocarbon lakes, together with the high solubility of N₂ in both methane and ethane [3] result in N₂ dissolution in surface liquids. The exact composition of Titan's liquids, however, is still poorly known. Vapor-liquid equilibrium calculations with activity models [4], Regular Solution Theory [5, 6] and Statistical Associating Fluid Theory [7] are some examples for approaches in use to estimate lake composition. Though, in the absence of extended datasets at Titan relevant temperature and pressure conditions, the used thermodynamic and kinetic parameters are often uncertain, extrapolated values. Using our recent work on experimental measurements of evaporation rates and liquid compositions under simulated Titan conditions [8, ref. lpsc abstract for mixtures], we present preliminary results on the thermodynamics and kinetics of N₂ dissolution in liquid hydrocarbons under cryogenic conditions relevant to Titan's surface.

Methods: The experiments were conducted in a facility specifically designed to simulate Titan's surface [10]. The simulation chamber is the same that has been used for previous experiments on hydrocarbon evaporation [e.g 8] and spectroscopy [11]. Titan relevant temperatures are achieved with flowing liquid nitrogen through various parts of the chamber, and a pressure of 1.5 bar is maintained with N₂ gas. Sample gases (C₂H₆ and CH₄) are then condensed and introduced into a petri dish connected to an electronic scale. Mass loss over time, along with the temperature, are continuously recorded over the course of the experiment.

In this work we use previous evaporation data obtained for pure CH₄ [8] and C₂H₆-CH₄ mixtures [9] and focus the study on the initial plateau section of the curves (Fig. 1) where N₂ dissolution is expected [9].

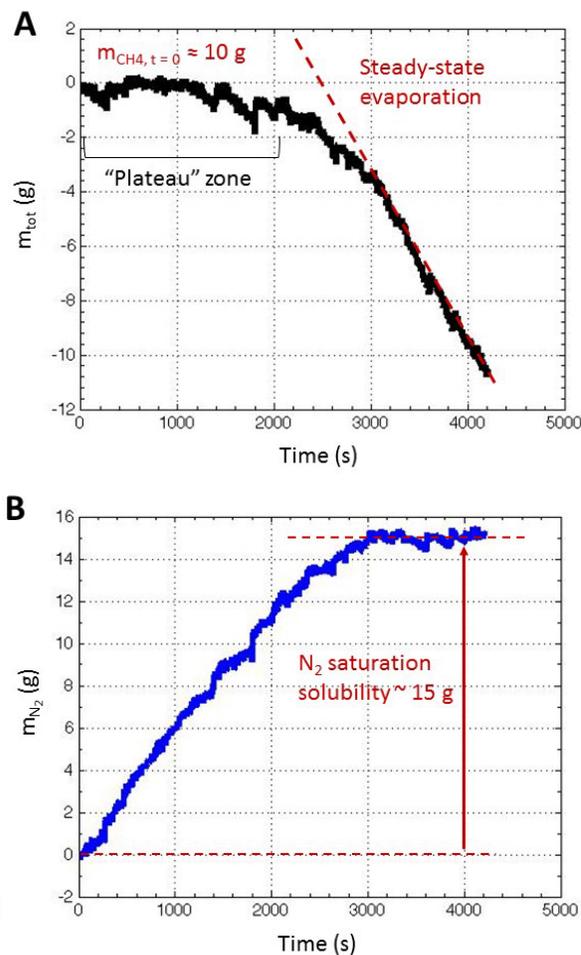


Figure 1: Experimental data for pure methane. **A.** Mass versus time showing the plateau zone after CH₄ pour, from 0 to 2000 s followed by the steady-state evaporation. **B.** Similar data after linear correction for the steady-state part. The increase of mass during the plateau zone is attributed to the dissolution of N₂ in liquid methane.

Results: To obtain a first order estimate on the amount of N₂ dissolving in liquid methane and ethane-methane mixtures, we make the following assumptions: 1. N₂ only dissolves in methane. While N₂ is soluble in both methane and ethane, it is ~ 5500 times more soluble in methane at 100 K and 1 bar [12]. Furthermore, there is no observable N₂ dissolution in the data for pure C₂H₆ liquid [9]; hence, we assume it is negligible compared to the role of methane. CH₄ evaporates with the same rate over the duration of the experiments. N₂ dissolution is then estimated from mass conservation, i.e. the amount of CH₄ evaporating is approximately equal to

the amount of N_2 dissolving, causing the horizontal plateau (Fig. 1A). Pure methane and mixture evaporation rates are determined from a least-square fit to the steady-state portion of the mass vs. time curves [8, 9] (Fig. 1A). Then the deviation from this initial evaporation rate (the plateau section) gives the theoretical amount of N_2 dissolved (Fig. 1B).

Initial $CH_4:C_2H_6$ mole fractions	Mole fraction of dissolved N_2	Average temperature of the liquid (K)	Average temperature of chamber atmosphere (K)
1.00:0.00	0.34	N/A	93.7
1.00:0.00	0.14	N/A	93.7
0.86:0.14	0.11	89.4	90.4
0.85:0.15	0.09	90.8	91.1
0.80:0.20	0.02	93.8	93.6
0.74:0.26	0.01	91.5	90.9
0.00:1.00	0.00		

Table 1. Amount of estimated N_2 dissolution in $CH_4-C_2H_6$ mixtures at various initial concentrations. Temperatures are averaged values over the duration of the plateau in each experiment.

Based on our preliminary study, there is a correlation between increasing methane concentration and the amount of N_2 dissolving (Table 1) from 1% at 74% CH_4 to 34% for pure methane. Though, there is some discrepancy in the obtained values between the same methane mole fractions, e.g. pure methane showing 14 and 34% dissolved N_2 (Table 1). Nevertheless, our results clearly show that N_2 is more soluble in methane than ethane. Such behavior would also explain why the evaporation rates of $CH_4-C_2H_6$ mixtures are systematically slower than predicted by pure binary mixture theory [9]

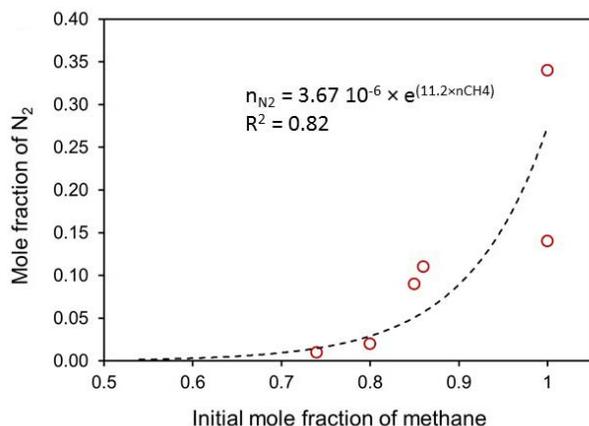


Figure 2. Mole fraction of dissolved nitrogen N_2 as a function of the initial mole fraction of methane in the mixture. We observe an exponential increase of N_2 solubility with increasing methane above 0.7 mole fraction of CH_4 .

Discussion: Various thermal processes are expected to occur over the part of the data this study is focused on, and the nature of the plateau is probably more complex than solely N_2 dissolution. Right after condensation, while N_2 is dissolving, the system is also attempting to reach equilibrium. Thermal transfer was shown to play a role in the case of pure methane experiments [8], which together with evaporative cooling would contribute to the plateau appearance of the initial portion of the mass vs. time curves. Furthermore, if methane is not thermally buoyant over the plateau region, it will not evaporate with the same rate as it does over the steady state part. Based on the combination of these effects and previous experimental results for pure methane [8], a scenario where N_2 dissolves faster than the time span of the plateau and the initial evaporation rate of CH_4 seems more plausible. In this case, methane and nitrogen would both evaporate (Fig. 1A) until a metastable equilibrium is reached.

These results are very important for current and future studies of Titan surface. Indeed it has been suggested that methane could undergo evaporative cooling due to its fast evaporation rate. However, N_2 could also act like an antifreeze. Alternatively, ethane evaporates very slowly and should not be subjected to evaporative cooling, although its freezing temperature is not affected by nitrogen. However, it is possible that some “ideal” mixture of methane and ethane could easily freeze on Titan, creating possible albedo variations on the surface [13].

Hence, the assumptions made in this study only allow us to provide an upper bound to the amount of N_2 being dissolved. Further detailed analysis will enable more accurate estimates of N_2 dissolution in Titan-relevant mixtures at cryogenic temperatures. Particularly, we will investigate if the solubility of N_2 is only function of the concentration of CH_4 or if C_2H_6 has an effect through ternary mixtures.

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