EVOLUTION OF TITAN'S ATMOSPHERE IN RELATION TO ITS SURFACE AND INTERIOR. A. E. Gilliam¹, A. Lerman¹, and J. Wunsch², ¹Department of Earth and Planetary Sciences, Northwestern University, Evanston IL, 60208-3130 (ashley@earth.northwestern.edu), ²Department of Mathematics, Northwestern University, Evanston IL, 60208-2730.

Introduction: Titan is the only known moon to have a thick atmosphere and the only world besides the Earth to have a liquid on its surface. In Titan's atmosphere, photochemistry of the methane (CH₄) molecule controls the composition of the atmosphere as well as the surface. In the upper atmosphere, direct and irreversible photolysis of methane principally produces ethane (C_2H_6) , which is subsequently condensed in the atmosphere and eventually accumulates on the surface. The irreversible destruction of methane by photolysis in, and its escape from, Titan's atmosphere suggest a much larger atmospheric methane budget on early Titan and a substantial surface liquid reservoir of ethane on present-day Titan. A careful investigation of the pathways of methane to ethane conversion throughout time could constrain the amount of ethane expected to be present on the surface of Titan, and give clues as to its subsurface composition.

CH₄ Depletion and C₂H₆ Production Through Time: In Titan's atmosphere, the production of all hydrocarbons commences with the photodissociation of methane. In the stratosphere, UV photolysis is responsible for $\sim 1/3$ of the total methane destruction [1], 75% of which occurs at the Lyman α wavelength (121.6 nm) [2]. At Lyman α , the photodissociation of methane is capable of producing other hydrocarbons, such as methyl radicals (CH₃). Once these hydrocarbons are formed they recombine to form heavier molecules (e.g. C₂H₆) that condense and eventually precipitate from the atmosphere. In Titan's atmosphere, ethane is the main photolysis product of methane [3], with a production rate of 1.3×10^8 molecules cm⁻² s⁻¹.

Another mechanism responsible for methane loss in the Titan atmosphere is hydrodynamic escape. First observed by the Voyager spacecraft and confirmed by the Cassini Ion Neutral Mass Spectrometer, the methane distribution in Titan's upper atmosphere remains uniformly mixed up to ~1100 km, where it begins to exhibit diffusive separation. Further evidence from the Cassini INMS suggested that methane is not well mixed to high altitudes because of a large escape rate.

Using a simplified model of Titan's atmosphere, we can calculate the amount of methane remaining as a function of time since accretion, and the subsequent production of ethane through photodestruction of the methane molecules. Expanding on our previous primordial atmospheric model [4], we assume a primordial atmospheric temperature of 300-355 K, an atmos-

pheric CH₄ mass of 1.19×10^{20} kg, and a scale atmosphere 128 km thick and top surface area of 9.18×10^{13} m². Under these conditions, we calculate that 8.46×10^{17} kg of atmospheric ethane should have been produced since accretion (~4.5 Ga). As a comparison, Ligeia Mare, the second largest lake on Titan (126,000 km²), is thought to contain ~5 × 10^{15} kg of hydrocarbons [5]. Assuming a liquid solution of 40% ethane [6], this corresponds to a mass of 2×10^{15} kg of liquid ethane. Our results predict a mass of ethane roughly $400 \times$ larger than observed in the second largest surface liquid reservoir on Titan, or $150 \times$ larger than its total hydrocarbons, suggesting a large quantity of liquid ethane in Titan's lakes and perhaps in Titan's subsurface.

CH₄-C₂H₆ in Titan's Atmosphere: 1st and 2nd Order Reaction Systems, Exact and Numerical Solutions of Simultaneous Equations: Simultaneous 1st and 2nd order chemical reactions occur in such systems as the transitions from CH_4 (1st order) $\rightarrow CH_3$ $(2nd order) \rightarrow C_2H_6$ (1st order) \rightarrow Other products, in the atmosphere of Titan. As far as we are aware, no exact mathematical solutions of the mixed 1st and 2nd order reaction systems are available in the literature. The novel exact solutions are for a case of the source species CH₄ with input from Titan's interior to its atmosphere. The exact solutions are compared to the approximations that are easier to handle in some cases. The results are based on the published and estimated values of the 1st and 2nd order reaction rate constants of the species. The rate and duration of CH₄ input to the atmosphere are uncertain because of the finite size of methane reservoir in the satellite interior, a feature often overlooked in mass balance calculations. The new exact solutions of the reactive system help to analyze evolution of Titan's atmosphere since its accretion and through subsequent cooling, and identify the rates of the different processes that are consistent with the present-day occurrences of methane and ethane in its atmosphere.

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