

AN ESTIMATE OF THE CHEMICAL COMPOSITION OF TITAN'S LAKES

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ABSTRACT

Hundreds of radar-dark patches interpreted as lakes have been discovered in the north and south polar regions of Titan. We have estimated the composition of these lakes by using the direct abundance measurements from the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe and recent photochemical models based on the vertical temperature profile derived by the Huygens Atmospheric Structure Instrument (HASI). Thermodynamic equilibrium is assumed between the atmosphere and the lakes, which are also considered as nonideal solutions. We find that the main constituents of the lakes are ethane (C₂H₆) (~ 76–79%), propane (C₃H₈) (~ 7–8%), methane (CH₄) (~ 5–10%), hydrogen cyanide (HCN) (~ 2–3%), butene (C₄H₈) (~ 1%), butane (C₄H₁₀) (~ 1%) and acetylene (C₂H₂) (~ 1%). The calculated composition of lakes is then substantially different from what has been expected from models elaborated prior to the exploration of Titan by the Cassini-Huygens spacecraft.

Subject headings: planets and satellites: individual: Titan – planets and satellites: general – solar system: general

1. INTRODUCTION

The surface of Saturn's haze-shrouded moon Titan had long been proposed to have oceans or seas, on the basis of the stability of liquid methane and ethane at the ground level (Flasar 1983; Lunine et al. 1983; Lorenz et al. 2003). Ground-based radar observations ruled out the presence of a global ocean in the 1990s (Muhleman et al. 1995), but the presence of isolated lakes was not precluded (Campbell et al. 2003). A large, dark, lake-like feature subsequently named Ontario Lacus was detected at Titan's south polar region by the Cassini ISS system in 2005 (McEwen et al. 2005) and hundreds of radar dark features with a variety of properties consistent with liquid-filled lakes were found in the northern hemisphere by the Cassini RADAR system (Stofan et al. 2007).

The chemical composition of the lakes of Titan is still not well determined. Good quality spectral data of the Ontario Lacus have been obtained by the Visual and Infrared Mapping Spectrometer (VIMS) aboard Cassini but the only species that seems firmly identified is C₂H₆ (Brown et al. 2008); the atmosphere contains so much CH₄ that it is very difficult to detect the surface liquid phase of this molecule even if it is dominant in the lakes. Because the detection of other compounds in the lakes of Titan remains challenging in the absence of in situ measurements, the only way to get a good estimate of the chemical composition of these lakes is to elaborate a thermodynamic model based on theoretical calculations and laboratory data. Several models, that investigate the influence of photochemistry and the atmospheric composition on the chemical composition of liquids formed on

the surface of Titan, have been elaborated in the pre-Cassini years (Lunine et al. 1983; Dubouloz et al. 1989; McKay et al. 1993; Tokano 2005). Based on atmospheric observations these models assumed surface bodies of liquid on Titan to contain a mixture of C₂H₆, CH₄ and N₂ and a large number of dissolved minor species.

TABLE 1
ASSUMED COMPOSITION OF TITAN'S ATMOSPHERE AT THE GROUND LEVEL.

Atmosphere	Mole fraction	Determination
H ₂	9.8×10^{-4}	Huygens GCMS ^(a)
N ₂	0.95	This work
CH ₄	0.0492	Huygens GCMS ^(b)
CO	4.70×10^{-5}	Cassini CIRS ^(c)
⁴⁰ Ar	4.32×10^{-5}	Huygens GCMS ^(b)
C ₂ H ₆	1.49×10^{-5}	This work

NOTE. — ^(a)Owen & Niemann 2009; ^(b)Niemann et al. 2005; ^(c)De Kok et al. 2007. N₂ and C₂H₆ abundances are determined from our model (see text).

However, Cassini-Huygens measurements have improved our knowledge of the structure and composition of Titan's atmosphere, requiring the solubilities to be re-computed under actual Titan conditions. In particular, the Gas Chromatograph Mass Spectrometer (GCMS) aboard Huygens and the Cassini Composite Infrared Spectrometer (CIRS) provided new atmospheric mole fraction data (see Table 1 and Niemann et al. 2005). Moreover, near-surface brightness temperatures at the high latitudes where the lakes exist have now been determined (Jennings et al. 2009).

Here, we propose a model that takes into account these recent advances and thus provides the most up-to-date chemical composition of Titan's lakes as a function of their location on the satellite's surface. Our model considers the same assumptions as those made by Dubouloz et al. (1989) (hereafter D89) when they calculated the composition of the hypothetical ocean proposed to exist on Titan in the years prior the Cassini-Huygens exploration. The lakes are then considered as

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nonideal solutions in thermodynamic equilibrium with the atmosphere. This assumption is supported by recent calculations who showed that raindrops could reach the ground in compositional equilibrium with the atmosphere (Graves et al. 2008).

2. THE MODEL OF LAKE-ATMOSPHERE EQUILIBRIUM

The general phenomenological picture of our model is the following: high altitude photochemistry produces gases and aerosols in Titan’s atmosphere, which are transported to lower altitude via atmospheric mixing, molecular diffusion, and sedimentation. At low temperature conditions found in the lower stratosphere and troposphere, the formed gases can condense on the aerosols and their precipitation rates (see Table 2). are given by photochemical models (Lavvas et al. 2008a, 2008b; Vuitton et al. 2008). From the different vapor pressures of the molecules that condense in Titan’s atmosphere, these models define the altitude (*i.e.* temperature) at which the condensation of each gas will start. Although the condensed phase can start as a liquid, the temperature of the surface is smaller than the temperature at the altitude where condensation begins for some of the molecules. This allows some of the condensables to reach the surface in the solid phase. The physical state of these precipitates as they enter the seas at Titan’s surface level does not matter as they are assumed to dissolve in thermodynamic equilibrium. The considered gas phase is representative of Titan’s atmosphere (see Table 1) and the ethane mole fractions in liquid and gas are considered as unknowns of the problem. Mole fractions of other species present in precipitation are supposed to have negligible gas phase abundances. We place our model in the framework of the regular solution theory. Thus, because the thermodynamic equilibrium is assumed between lakes and atmosphere, the equality of chemical potentials for each species listed in Table 1 can be written as (Eq. 1 of D89):

$$Y_i P = \Gamma_i X_i P_{vp,i}, \quad (1)$$

where P is the total pressure at Titan’s surface, Y_i and X_i are respectively the mole fractions of the i compound in the atmosphere and the liquid, $P_{vp,i}$ its vapor pressure, and Γ_i its activity coefficient in the liquid given by Eq. 2 of D89. Abundances of compounds below C_2H_6 in Table 2 are expressed proportionally to that of C_2H_6 both in the precipitation and in the lakes. Because the system of involved equations is non-linear, it is solved with the use of the Newton Raphson’s method.

Our model also allows us to estimate the fractions of solid precipitates that can be dissolved in the lakes of Titan. To this end, we calculate the *saturation* mole fraction⁷ $X_{i,sat}$ of the i compound, which is given by (Eq. 7 of D89):

$$\ln(\Gamma_i X_{i,sat}) = (\Delta H_m / RT_m)(1 - T_m/T), \quad (2)$$

where T_m is the component’s melting temperature and ΔH_m its enthalpy of fusion. Our calculation procedure is then conducted as follows:

⁷ The saturation mole fraction of the i compound corresponds to the maximum mole fraction of i in the liquid form. Above this value, the i material in excess remains in solid form.

1. The unknown X_i ’s and Y_i ’s are computed via the Newton-Raphson method.
2. Once the X_i ’s have been determined, the $X_{i,sat}$ ’s are in turn calculated and compared to the X_i ’s for each species. If for compound i we get $X_{i,sat} < X_i$, then we fix $X_i = X_{i,sat}$.
3. We get new values of X_i ’s and $X_{i,sat}$ ’s via the resolution of the nonlinear system.
4. The iterations are continued until we get a difference between $X_{i,sat}$ and X_i lower than 10^{-6} , value for which the numerical inaccuracy is clearly negligible compared to other sources of uncertainties.

The known Y_i ’s are given in Table 1. The precipitation rates used here are given in Table 2 and derive from the photochemical models of Lavvas et al. (2008a,b) and Vuitton et al. (2008) and correspond to the main products of CH_4 and N_2 photolysis. These rates allow to express each i compound that precipitates in the form $X_i = \frac{\tau_i}{\tau_{C_2H_6}} \times X_{C_2H_6}$. We also ensure that $\sum_i X_i = 1$ and $\sum_i Y_i = 1$. The thermodynamic data used in our calculations derive from the NIST database⁸ when they are available and the remaining ones have been taken from D89. Note that H_2 is the only compound whose mole fraction in the liquid is not determined with the aforementioned procedure. Instead, we calculate the amount of dissolved H_2 in the liquid via Henry’s law (D89).

TABLE 2
PRECIPITATION RATES (τ) ASSUMED AT THE GROUND LEVEL.

	Compound	Rate τ ($cm^{-2} s^{-1}$)
Liquids	C_2H_6	$3.4 \times 10^9^{(a)}$
	C_3H_8	$3.3 \times 10^8^{(a)}$
	C_4H_8	$6.2 \times 10^7^{(a)}$
Solids	HCN	$1.3 \times 10^8^{(a)}$
	C_4H_{10}	$5.4 \times 10^7^{(a)}$
	C_2H_2	$5.1 \times 10^7^{(a)}$
	CH_3CN	$4.4 \times 10^6^{(a)}$
	CO_2	$1.3 \times 10^6^{(a)}$
	C_6H_6	$1.0 \times 10^6^{(b)}$

NOTE. — ^(a)Lavvas et al. (2008a, 2008b); ^(b)Vuitton et al. (2008).

3. RESULTS

Our calculations in the framework of thermodynamic equilibrium have been performed for two different regions of Titan’s surface. The first zone corresponds to the vicinity of the landing site of the Huygens probe, where the surface temperature was measured to be 93.65 K (Niemann et al. 2005). The Huygens probe detected drainage-like features and a high surface relative humidity, so the presence of liquids cannot be excluded in this area (Tomasko et al. 2005; Niemann et al. 2005). The second zone corresponds to the north pole of Titan where

⁸ <http://webbook.nist.gov>

the surface temperature is around ~ 90 K based on near-surface brightness temperature measurements (Jennings et al. 2009). In both cases, the atmospheric pressure is assumed to be identical and corresponds to that (1.46 bar) measured by Huygens at the ground level (Niemann et al. 2005).

Figure 1 shows the variation of the composition of Titan's lakes as a function of the surface temperature. It appears that the mole fractions of CH_4 , N_2 , CO and Ar decrease with the increase of temperature, while the mole fraction of C_2H_6 and of the precipitates increase. This is due to the vapor pressure of C_2H_6 , whose temperature dependence is lower than those of CH_4 , N_2 , CO and Ar . Figure 2 displays the variation of the composition of the lakes of Titan as a function of the atmospheric CH_4 mole fraction at the ground level, assuming a surface temperature of 93.65 K. It shows that an increase of the CH_4 atmospheric mixing ratio enhances its corresponding mole fraction in the liquid, as well as those of N_2 , CO and Ar . Interestingly enough, HCN is the only compound reaching saturation within the considered ranges of temperature and atmospheric methane mole fraction. Indeed, the HCN mole fraction represented as a function of the soil temperature in figure 1 panel (e) corresponds to the saturation limit for any temperature lower than 94.5 K (change of the curve's slope). This is due to the solubility of this compound diminishing with decreasing temperature. Moreover, figure 2 panel (c) shows that when Y_{CH_4} is larger than ~ 0.04 , the lake is saturated in HCN . Because it is more dense than the liquid⁹, the non-dissolved HCN should sink in the lakes of Titan.

Table 3 gives the mole fractions of the main compounds in lakes formed on the surface of Titan and shows that, whatever the considered site, their composition is dominated by C_2H_6 , C_3H_8 , CH_4 , HCN , C_4H_8 , C_4H_{10} and C_2H_2 . On the other hand, with mole fractions much lower than 1%, N_2 , C_6H_6 , CH_3CN , CO_2 , Ar , CO and H_2 are found to be minor compounds in the lakes.

4. DISCUSSION

The use of more up-to-date thermodynamic data and the recent Cassini-Huygens measurements, results in our calculated composition of the lakes differing from that of the hypothetical global ocean determined by D89. Indeed, considering the D89 case most closely corresponding to actual Titan conditions ($T = 92.5$ K, $Y_{\text{Ar}} = 0$ and $Y_{\text{CH}_4} = 0.0492$; see their Fig. 1), they obtained mole fractions of C_2H_6 , CH_4 and N_2 of ~ 0.35 , 0.60 and 0.05 , respectively. The most striking difference in the comparison is that the mole fraction of N_2 is more than 10 times lower in our results than in theirs, and some compounds considered as minor in the ocean of D89 are not negligible in the composition of our lakes. However, our model reproduces the results of D89 when we adopt precisely the same thermodynamic parameters. The fact that relatively small differences (order of a few percent) between our thermodynamic data extracted from the NIST database and those of D89 lead to significantly different results illustrates the non-linearity of the system of equations determining the composition of the liquid. It is difficult to quantify the errors on the predicted mole frac-

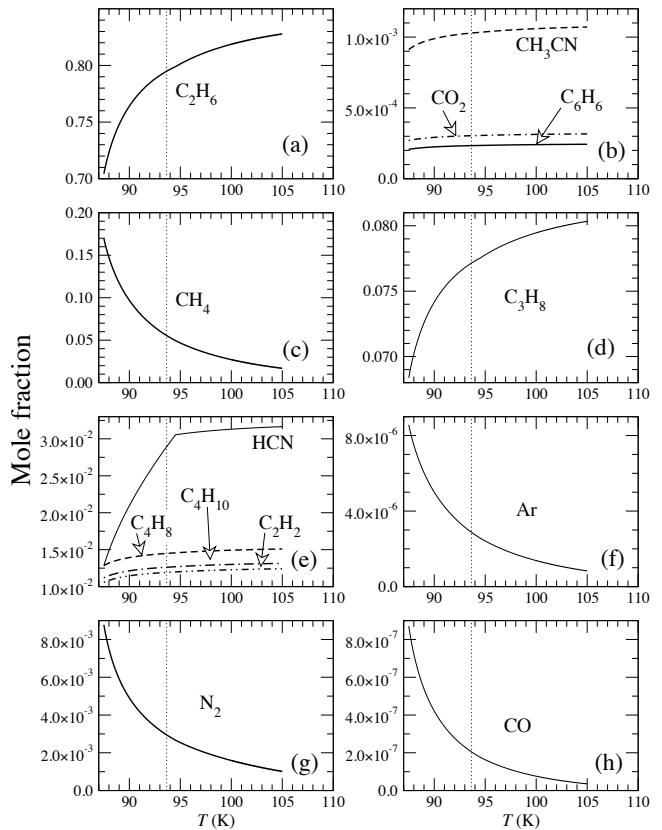


FIG. 1.— (a)–(h): composition of lakes as a function of the surface temperature. The vertical dashed line corresponds to the surface temperature of 93.65 K measured by Huygens.

tions of the different species because our model is based on thermodynamic data much of which is provided either without uncertainties or is derived from extrapolation of data to low temperature. However, numerical tests aiming to investigate the sensitivity of our model to the photochemical models we employ indicate that a $\pm 30\%$ variation of the C_2H_6 precipitation rate induces similar variations for the C_3H_8 to C_6H_6 lake mole fractions but poorly alters the N_2 to C_2H_6 lake mole fractions given in Table 3. Moreover, as shown by Fig. 2, a variation of the methane atmospheric abundance hardly affects the lake mole fractions of the precipitates. Pure numerical errors due to the algorithm have been estimated absolutely negligible.

We also outline that the assumption of thermodynamic equilibrium between the lakes and the atmosphere is a crude approximation since in fact the humidity and temperature of the atmosphere in contact with the lakes is determined by dynamic processes such as convection and wind advection (Mitri et al. 2007).

Our solubility calculations imply that a number of species produced by methane photolysis and energetic particle chemistry in Titan's upper atmosphere should be readily detectable with a mass spectrometer carried to the surface of a liquid-filled lake by a Huygens-like entry probe (Coustenis et al. 2009). The measured abundances of multiple minor constituents in the lake, coupled to measurements and models of stratospheric abundances and production rates, and direct temperature measure-

⁹ The mean molar volume of the liquid HCN is 4.8×10^{-5} m³/mol while that of solid HCN is lower than 3.8×10^{-5} m³/mol.

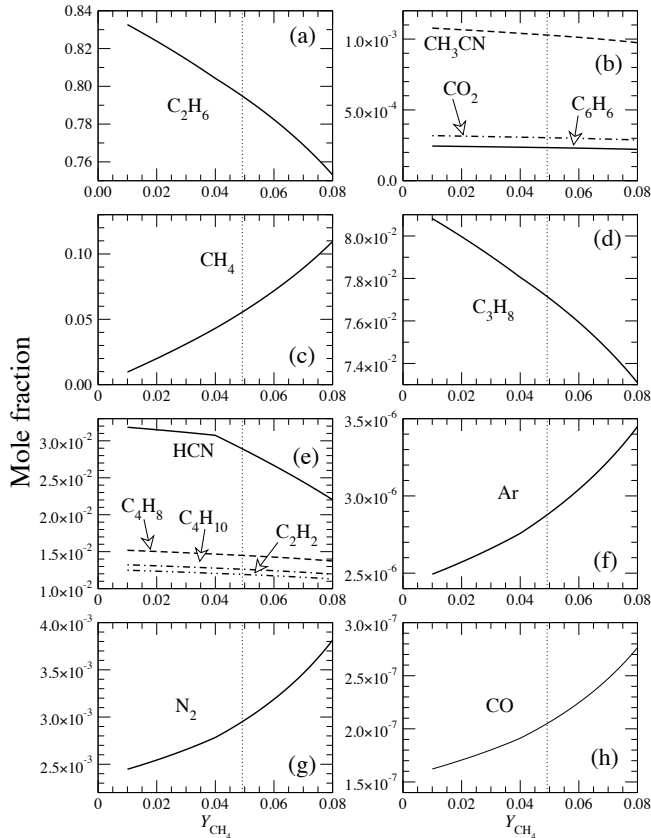


FIG. 2.— (a)–(h): composition of lakes as a function of the methane atmospheric mole fraction, assuming a surface temperature of 93.65 K. The vertical dashed line corresponds to the methane atmospheric mole fraction measured by Huygens at the ground level.

ments of the lake surface, will constrain lake properties that are of interest in understanding the methane hydrologic cycle. For example, at the winter pole a seasonally deposited upper-layer of liquid methane might exist on top of a longer-lived ethane-methane liquid reservoir by virtue of methane’s lower density and limited vertical mixing in the cold lakes (Stevenson and Potter 1986). Such a transient layer would be bereft of minor components compared with our values thanks to the slow sedimentation rate of the high altitude aerosols compared to the seasonal (meteorological) methane deposition rate; our solubility values provide a means of calculating the extent to which the longer-lived liquid reservoir below has mixed into the methane meteorological layer. (The extreme cold of the tropopause of Titan prevents the hydrocarbon constituents other than methane and possibly ethane from passing directly to the lower atmosphere in the gas phase; thus the lakes must be seeded by stratospheric aerosol sedimentation).

A longer-lived ethane-methane lake sampled at the summer pole might still have undergone pole-to-pole

transport on timescales of tens of millenia thanks to the precession of perihelion of Saturn’s orbit around the Sun (Aharonson et al. 2009). The abundances of minor constituents compared to our values which assume accumulation over geologic time, coupled with the aerosol sedimentation rate, could be used to “date” the liquid reservoir and hence test whether they have been cycled on

TABLE 3
CHEMICAL COMPOSITION OF LAKES AT THE POLES AND THE EQUATOR.

	Equator (93.65 K)	Poles (90 K)
Main composition (lake mole fraction)		
N ₂	2.95×10^{-3}	4.90×10^{-3}
CH ₄	5.55×10^{-2}	9.69×10^{-2}
Ar	2.88×10^{-6}	5.01×10^{-6}
CO	2.05×10^{-7}	4.21×10^{-7}
C ₂ H ₆	7.95×10^{-1}	7.64×10^{-1}
C ₃ H ₈	7.71×10^{-2}	7.42×10^{-2}
C ₄ H ₈	1.45×10^{-2}	1.39×10^{-2}
H ₂	5.09×10^{-11}	3.99×10^{-11}
Solutes (lake mole fraction)		
HCN	2.89×10^{-2} (s)	2.09×10^{-2} (s)
C ₄ H ₁₀	1.26×10^{-2} (ns)	1.21×10^{-2} (ns)
C ₂ H ₂	1.19×10^{-2} (ns)	1.15×10^{-2} (ns)
C ₆ H ₆	2.34×10^{-4} (ns)	2.25×10^{-4} (ns)
CH ₃ CN	1.03×10^{-3} (ns)	9.89×10^{-4} (ns)
CO ₂	3.04×10^{-4} (ns)	2.92×10^{-4} (ns)

NOTE. — (s): saturated; (ns) non saturated.

the “Milankovitch” timescale. For species that are chemically inactive and occur as gas only in the atmosphere, such as the noble gases, the lakes provide a second reservoir other than the atmosphere to measure abundances. Variations from the atmospheric value of, for example, ⁴⁰Ar/³⁶Ar, might hint at contact between the lakes and a much deeper crustal reservoir of liquid methane and ethane not in contact with the atmosphere (Hayes et al. 2008). Finally, our results provide the chemical data needed to compute the amount of deposition of various hydrocarbons and nitriles in fluvial valleys in the Titan’s midlatitudes, as a function of the flow of methane runoff from convective storms, allowing potential tests of models of fluvial erosion (Perron et al. 2006).

This work was supported in part by the CNES. Support from the PID program “Origines des Planètes et de la Vie” of the CNRS, and the *Cassini* project, are also gratefully acknowledged. We acknowledge Bruno Bézard, Sébastien Lebonnois and Pascal Rannou for helpful discussions about Titan’s atmosphere. We thank John Prausnitz for providing us with some unpublished thermodynamic data. We thank an anonymous reviewer for his constructive comments which helped us improve our manuscript.

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