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The Atmosphere and Internal Structure of Saturn's Moon Titan, a Thermodynamic Study

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1. Introduction

The atmosphere and internal structure of the icy satellites of Jupiter and Saturn offer a most interesting subject of studying their thermodynamic properties. The treatment provides a motivating example of applying thermodynamic and physical principles beyond the well known classical areas of chemical engineering and chemical separation or reaction processes. Particularly Saturn's largest moon Titan is most suitable for that purpose for several reasons. There exist numerous data of Titan obtained by observations from Earth, from the Voyager 1 and 2 missions in 1977 and more recently from the Cassini-Huygens mission which in particular provided most spectacular results in the years 2005 to 2008:

- Titan has a dense atmosphere consisting mainly of N_2 (93 – 98 %) and methane (7 – 2 %) with a pressure of 1.5 bar and a temperature of $-180^\circ C = 93 K$ at the bottom.
- Methane plays a similar role on Titan as water on Earth causing similar meteorological processes.
- Liquid lakes consisting of the atmospheric components cover at least 4 % of Titan's surface, maybe even more, because only parts of Titan's surface have been investigated so far by the Cassini probe.
- Solid water ice plays a similar role as rocky material and sediments on Earth's surface.
- Due to its low density ($1.88 g \cdot cm^{-3}$) Titan must contain remarkable amounts of water in its mantle while its inner core consists of rocky material.

Important questions arise which can be answered by thermodynamic methods as shown in the following sections:

- What is the composition of the condensed liquid phase on Titan's surface?
- What does the temperature profile of the atmosphere look like and what role does methane play in the formation of clouds and rainfall?
- How have the atmosphere and surface developed in the past and what will be their future fate?
- What can be said about Titan's internal structure?

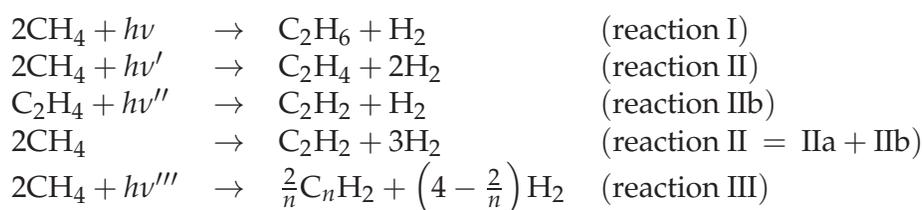
Table 1 gives some information on physical properties and interplanetary data of Titan. Titan always turns the same side to Saturn, i. e., its rotational period is identical with its revolution time around Saturn. Much more detailed information than presented in this

article can be found in the literature (Atreya et al., 2006; Barth & Toon, 2003; Flasar et al., 2005; Fulchignoni et al., 2005; Griffith et al., 2006; Lewis, 1997; Lorenz et al., 1997; 2008; Mitri et al., 2007; Mousis & Schmitt, 2008; Niemann et al., 2005; Rannou et al., 2006; Stofan et al., 2007; Yung & DeMore, 1999; Yung et al., 1984).

2. Photochemistry in Titan's atmosphere

The most important gaseous components detected and determined quantitatively in Titan's atmosphere are presented in Table 2.

The atmosphere is characterized by clouds in the troposphere and a hazy upper atmosphere containing aerosol particles of $\sim 1\mu$ m size which conceals a free view to Titan's surface in the visible region of light. However, UV, IR and mainly radar imaging technique is able to reveal details of Titan's atmosphere and surface. This situation indicates an intensive photochemical activity in the atmosphere. A simplified version of the photochemical destruction processes caused by solar UV-irradiation reads as follows (Atreya et al., 2006; Lorenz et al., 1997; Yung et al., 1984; Yung & DeMore, 1999)



This reaction scheme shows that the appearance of C_2H_6 and C_2H_2 in the atmosphere (s. Table 2) has its origin in the photochemistry of CH_4 . C_2H_4 is a photochemically unstable intermediate product. The haze in the upper atmosphere is mainly caused by the production of polyenes (reaction III). H_2 escapes rapidly from the atmosphere into the space due to Titan's low escape velocity. It is assumed that ca. 80 % of the destructed CH_4 is transformed into C_2H_6 , ca. 12 % into C_2H_2 and 8 % into polyenes (Yung & DeMore, 1999; Griffith et al., 2006). C_2H_6 is assumed to be dissolved partly in the liquid lakes on the surface. Most of C_2H_6 and all other photochemical products remain as small particles in the atmosphere (polyenes) or are adsorbed on the icy surface on the bottom.

3. The composition of lakes on Titan's surface

The discovery of liquid lakes with areas up to the size of Lake Superior (USA) was one of the most spectacular results of the Cassini mission (Stofan et al., 2007; Mitri et al., 2007; Lorenz et al., 2008). What is the composition of these lakes covering at least several percent of the surface? The most simple assumption is that these lakes consist of a liquid mixture of N_2 and CH_4 , which are also the dominant components in the gaseous atmosphere. It is an easy task to calculate the liquid composition treating the binary system as an ideal liquid mixture. We only have to know the temperature of the lakes and the saturation pressure.

mass/kg	radius/km	gravity acceleration/ $\text{m} \cdot \text{s}^{-2}$	average density/ $\text{g} \cdot \text{cm}^{-3}$	rotational period/days
$1.344 \cdot 10^{23}$	2575	1.354	1.88	16
surface temperature/K	surface pressure/bar	surface area/ m^2	distance to sun/km	distance to Saturn/km
93	1.49	$8.332 \cdot 10^{13}$	$1.428 \cdot 10^9$	$1.222 \cdot 10^6$

Table 1. Physical parameters of Titan.

N ₂	CH ₄	H ₂	CO	C ₂ H ₆	C ₂ H ₂	C ₂ H ₄	HCN
93–98	7–2	0.1	6 · 10 ⁻³	2 · 10 ⁻³	2 · 10 ⁻⁴	4 · 10 ⁻⁵	2 · 10 ⁻⁵

Table 2. Atmospheric composition in mol % (Yung & DeMore, 1999)

Obvious choices are the experimentally determined surface temperature of $T = 93$ K and the total surface pressure $p = 1.49$ bar. According to Raoult's ideal law it follows

$$p \cdot y_{\text{CH}_4} = p_{\text{CH}_4}^{\text{sat}} \cdot x_{\text{CH}_4} \quad \text{and} \quad p \cdot y_{\text{N}_2} = p_{\text{N}_2}^{\text{sat}} (1 - x_{\text{CH}_4}) \quad (1)$$

with the molefractions y_i and x_i in the gaseous atmosphere and in the liquid phase respectively ($i = \text{CH}_4, \text{N}_2$).

The saturation pressures of methane and nitrogen at 93 K are (Prydz & Goodwin, 1972; Wagner & de Reuck K. M., 1996; Span et al., 2001):

$$p_{\text{CH}_4}^{\text{sat}} = 0.1598 \text{ bar}, \quad p_{\text{N}_2}^{\text{sat}} = 4.625 \text{ bar}$$

Using these data we obtain

$$x_{\text{CH}_4} = \frac{p - p_{\text{N}_2}^{\text{sat}}}{p_{\text{CH}_4}^{\text{sat}} - p_{\text{N}_2}^{\text{sat}}} = 0.698 \quad \text{and} \quad x_{\text{N}_2} = 1 - x_{\text{CH}_4} = 0.302 \quad (2)$$

The predicted composition of the atmosphere is therefore

$$\begin{aligned} y_{\text{CH}_4} &= p_{\text{CH}_4}^{\text{sat}} \cdot x_{\text{CH}_4} / p = 0.074 \\ y_{\text{N}_2} &= p_{\text{N}_2}^{\text{sat}} \cdot x_{\text{N}_2} / p = 0.926 \end{aligned} \quad (3)$$

This is close to the experimental data of y_{N_2} (0.93 – 0.98) and y_{CH_4} (0.02 – 0.07) and suggests that the predicted composition of the lakes with 70 mole percent CH₄ and 30 mole percent N₂ is no unreasonable result.

However, there exist serious arguments in the literature that the liquid phase of the lakes and also humidity in the pores of the solid water ice on the bottom may contain also considerable amounts of ethane (C₂H₆) (Lorenz et al., 2008; Barth & Toon, 2003; Rannou et al., 2006; Griffith et al., 2006; Mousis & Schmitt, 2008) since C₂H₆ is soluble in liquid CH₄ or liquid CH₄ + N₂ mixtures. Therefore a more refined model of the ternary system CH₄ + N₂ + C₂H₆ has to be applied accounting also for non-ideality of the three mixture components in the liquid as well as in the gaseous phase.

We start with the following expression for the total pressure p of a real liquid ternary mixture being in thermodynamic equilibrium with its real gaseous phase ($C = \text{CH}_4, N = \text{N}_2, E = \text{Ethan} = \text{C}_2\text{H}_6$).

$$p = (x_C \gamma_C) \cdot (\pi_C \cdot p_C^{\text{sat}}) + (x_N \gamma_N) \cdot (\pi_N \cdot p_N^{\text{sat}}) + (x_E \gamma_E) \cdot (\pi_E \cdot p_E^{\text{sat}}) \quad (4)$$

γ_i ($i = C, N, E$) and π_i ($i = C, N, E$) are the activity coefficients of i in the liquid phase and the so-called Poynting correction factors for component i respectively. Eq. (4) exhibits a sufficiently correct description of ternary vapor-liquid phase equilibria provided the reality of the gaseous phase can be described by accounting for second virial coefficients B_i and the approximation is acceptable that all activity coefficients in the vapor phase are unity (Lewis-Randall rule in the vapor phase).

γ_i and π_i are given by the following equations:

$a_{CN}/J \cdot mol^{-1}$	$a_{CE}/J \cdot mol^{-1}$	$a_{NE}/J \cdot mol^{-1}$
720	440	800
$\bar{V}_{CH_4}^l/cm^3 \cdot mol^{-1}$	$\bar{V}_{N_2}^l/cm^3 \cdot mol^{-1}$	$\bar{V}_{C_2H_6}^l/cm^3 \cdot mol^{-1}$
35.65	38.42	67.83
$B_{CH_4}/cm^3 \cdot mol^{-1}$	$B_{N_2}/cm^3 \cdot mol^{-1}$	$B_{C_2H_6}/cm^3 \cdot mol^{-1}$
-455	-186	-2500

Table 3. Thermodynamic parameters of the ternary mixture components at 93 K

$$\begin{aligned}
 RT \ln \gamma_C &= a_{CN} \cdot x_N(1 - x_C) + a_{CE}(1 - x_C)x_E - a_{NE}x_N \cdot x_E \\
 RT \ln \gamma_N &= a_{CN} \cdot x_C(1 - x_N) + a_{NE}(1 - x_N)x_E - a_{CE}x_C \cdot x_E \\
 RT \ln \gamma_E &= a_{CE} \cdot x_C(1 - x_E) + a_{NE}(1 - x_E)x_N - a_{CN}x_C \cdot x_N
 \end{aligned} \tag{5}$$

with the balance for mole fractions

$$x_C + x_N + x_E = 1$$

and the Poynting factors

$$\pi_i = \exp \left[\frac{(\bar{V}_{i,l} - B_i)(p - p_i^{\text{sat}})}{RT} \right] \quad (i = C, N, E) \tag{6}$$

The parameters a_{ij} characterize the difference of intermolecular interactions in binary liquid mixtures $i + j$ and are based on the simple expression for the molar Gibbs excess enthalpy G_{ij}^E of the binary mixture $i + j$:

$$G_{ij}^E = a_{ij} x_i x_j$$

The Gibbs excess enthalpy of the ternary mixture is

$$G_{\text{ter}}^E = RT(x_C \ln \gamma_C + x_N \ln \gamma_N + x_E \ln \gamma_E) \tag{7}$$

with $\ln \gamma_i$ from eq. (5).

Parameters a_{CN} , a_{CE} and a_{NE} can be obtained from experimental data of binary G_{ij}^E available from the literature (Miller et al., 1973; McClure et al., 1976; Ponte et al., 1978) by fitting eq. (7) to the experiments. Values obtained are listed in Table 3. Calculation of π_i in eq. (6) requires data of the liquid molar volume \bar{V}_i^l (Liu & Miller, 1972; Massengill & Miller, 1973) and the second virial coefficient B_i (Span et al., 2001; Bucker & Wagner, 2006; Wagner & de Reuck K. M., 1996) for each component at $T = 93$. Values are also listed in Table 3.

At given liquid composition x_C, x_N and $x_E = 1 - x_C - x_N$, γ_C, γ_N and γ_E can be calculated using eq. (5). π_C, π_N and π_E can be calculated by eq. (6) using $p = 1.49 \cdot 10^5$ Pa and the known values of p_i^{sat} . Compositions $y_i (i = C, N, E)$ are then obtained by

$$y_i = x_i \gamma_i p_i^{\text{sat}} \cdot \pi_i \quad (i = C, N, E) \tag{8}$$

It turns out that $y_E \approx 0$ for almost all compositions x_C and x_N due to the negligible vapor pressure $p_E^{\text{sat}} = 2.3 \cdot 10^{-5}$ bar (Bucker & Wagner, 2006) compared to p_C^{sat} and p_N^{sat} at 93 K. As a result the vapor phase can be treated as a binary mixture of CH_4 and N_2 . For presenting

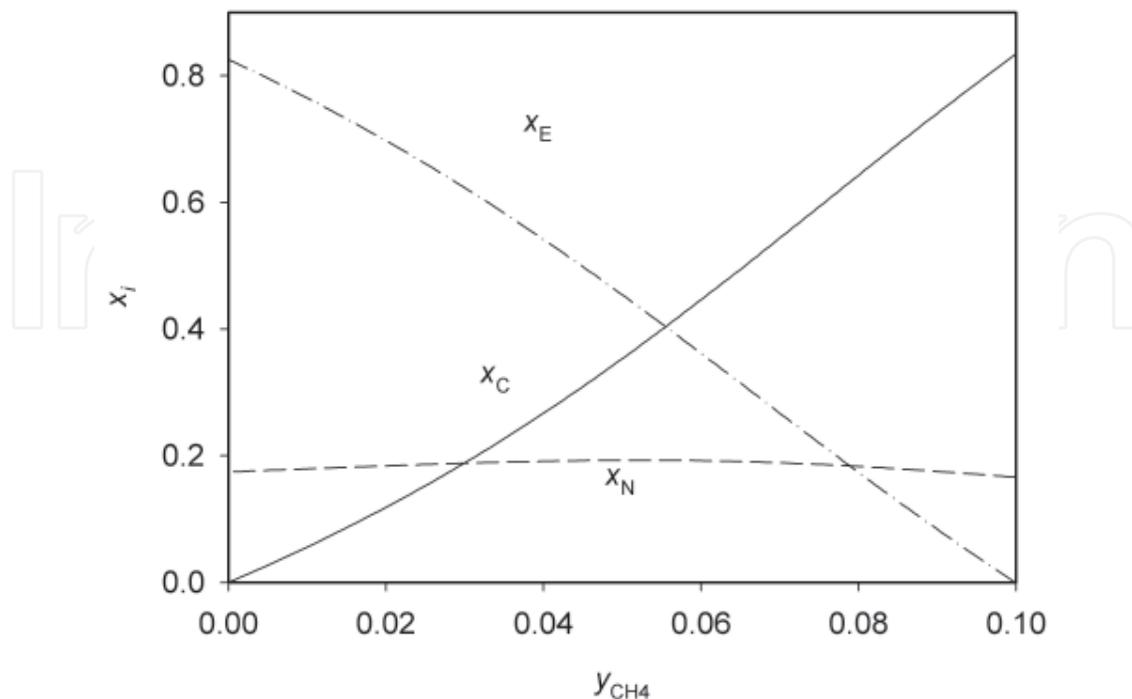


Fig. 1. Liquid composition x_i ($i = C, N, E$) of the ternary system $\text{CH}_4 + \text{N}_2 + \text{C}_2\text{H}_6$ as function of molfraction of methane, y_C , in a saturated atmosphere

our results of the ternary liquid mixture in Fig. 1 the mole fractions in the liquid state x_C, x_N and $x_E = 1 - x_C - x_N$ are plotted as function of the composition of $y_{\text{CH}_4} \cong 1 - y_{\text{N}_2}$ up to $y_{\text{CH}_4} = 0.1$. Fig. 1 shows that x_E is continuously decreasing with increasing y_C while x_C is continuously increasing. At $y_{\text{CH}_4} \cong 0.10, x_E = 0$, i. e. values of $y_{\text{CH}_4} \geq 0.1$ would indicate that no ethane can be present in the liquid phase. Interestingly x_N is almost independent of y_C with values close to 0.18. The following conclusions can be drawn from Fig. 1. Since experimental values of y_{CH_4} lie between 0.02 and 0.07 the results suggest that ethane would be present in the liquid phase with values of x_E in the range of 0.7 to 0.2. However, there is no evidence that the measured values of y_{CH_4} are really values being in thermodynamic equilibrium with a saturated liquid mixtures at the places where these values have been measured in Titan's atmosphere. Therefore equilibrium values of y_{CH_4} which are representative for the liquid composition of the lakes may reach or even exceed 0.1. In this case most likely no ethane would be present in the lakes and the liquid composition would be $x_{\text{CH}_4} \cong 0.834$ and $x_{\text{N}_2} \cong 0.166$ which is different from the result obtained by eq. (2) under the assumption of an ideal binary mixture ($x_{\text{CH}_4} = 0.698, x_{\text{N}_2} = 0.302$).

4. Cloud formation and rainfall in Titan's troposphere

Early attempts to describe quantitatively the situation of a saturated atmosphere of Titan can be found in the literature (Kouvaris & Flasar, 1991; Thompson et al., 1992). We provide here a simple and straight forward procedure based on the most recent results of the temperature profile of the lower atmosphere.

Fig. 2 shows the temperature profile of Titan's atmosphere as measured by the landing probe Huygens (Fulchignoni et al., 2005). The relatively high temperatures in the thermosphere

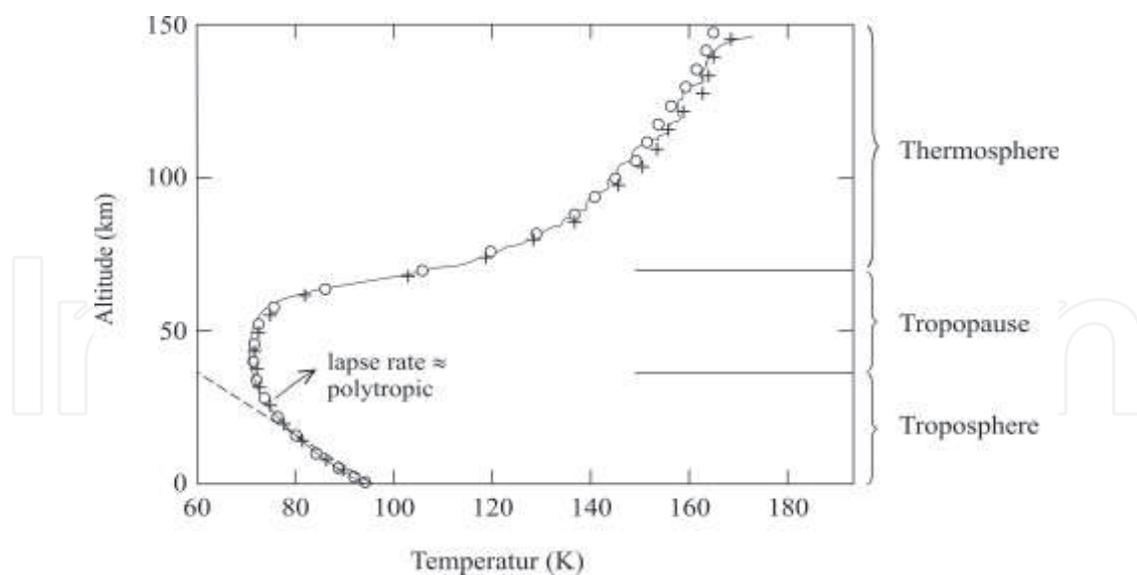


Fig. 2. Temperature profile in Titan's atmosphere (see text).

are caused by the absorption of solar radiation. This is the region where the photochemical processes take place. At ca. 40 km the temperature reaches a minimum value of ca. 73 K increasing again below this altitude. The nearly linear temperature profile below 20 km is called the polytropic lapse rate. Its slope (dT/dh) is negative ($-0.92 \text{ K} \cdot \text{km}^{-1}$). This is the part of the troposphere where cloud formation of $\text{CH}_4 + \text{N}_2$ -mixtures can take place as well as rainfall. Such negative lapse rates of temperature are also observed in other dense atmospheres, e. g. on the Earth or on the Venus and can be explained by the convection of gases in a gravitational field which corresponds approximately to an isentropic process which is given by the following differential relationship valid for ideal gases:

$$\frac{dT}{T} = \frac{\gamma - 1}{\gamma} \frac{dp}{p} \quad \text{with } \gamma = C_p/C_V \quad (9)$$

C_p and C_V are the molar heat capacities at constant pressure and volume respectively. Real processes are often better described by ε instead of γ with

$$1 \leq \varepsilon \leq \gamma \quad (10)$$

ε is called the polytropic coefficient.

Considering hydrostatic equilibrium as a necessary condition in any atmosphere we have for ideal gases:

$$dp = -p \frac{\bar{M} \cdot g}{RT} dh \quad (11)$$

where \bar{M} is the average molar mass of the gas and h is the altitude.

Combining eq. (9) with eq. (11) and using ε instead of γ integration gives the temperature profile in the atmosphere

$$T(h) = T_0 \left(1 - \frac{\bar{M} \cdot g}{R} \frac{\varepsilon - 1}{\varepsilon} \frac{h}{T_0} \right) \quad (12)$$

with $\bar{M} = 0.028 \text{ kg} \cdot \text{mol}^{-1}$, $T_0 = 93 \text{ K}$ and $g = 1.354 \text{ m} \cdot \text{s}^{-2}$ (see Table 1).

Substituting eq. (12) into eq. (9) integration gives the pressure profile in the atmosphere:

$$p(h) = p_0 \left(1 - \frac{\bar{M} \cdot g}{R} \frac{\varepsilon - 1}{\varepsilon} \frac{h}{T_0} \right)^{\frac{\varepsilon}{\varepsilon - 1}} = p_0 \left(\frac{T(h)}{T_0} \right)^{\frac{\varepsilon}{\varepsilon - 1}} \quad (13)$$

with $p_0 = 1.49 \cdot 10^5$ Pa.

The experimental lapse rate $(dT/dp) = -0.92 \text{ K} \cdot \text{km}^{-1}$ is best described by eq. (12) with $\varepsilon = 1.25$. It is worth to note that eq. (13) gives the barometric formula for an isothermic atmosphere with $T = T_0$ in the limiting case of $\lim_{\varepsilon \rightarrow 1}$ [eq. (13)].

We are now prepared to develop a straightforward procedure for calculating cloud formation based on the assumption of a real binary mixture in the liquid state consisting of CH_4 and N_2 . By equating eq. (4) with $x_{\text{Ethane}} = 0$ and eq. (13) we obtain:

$$\begin{aligned} p(h) &= x_{\text{CH}_4} \cdot \gamma_{\text{CH}_4} \cdot \pi_{\text{CH}_4} \cdot p_{\text{CH}_4}^{\text{sat}}(T(h)) + (1 - x_{\text{CH}_4}) \cdot \gamma_{\text{N}_2} \pi_{\text{N}_2} \cdot p_{\text{N}_2}^{\text{sat}}(T(h)) \\ &= p_0 \left[1 - \frac{\bar{M} \cdot g}{R} \cdot \frac{\varepsilon - 1}{\varepsilon} \frac{h}{T_0} \right]^{\varepsilon/(\varepsilon - 1)} \end{aligned} \quad (14)$$

Substituting now $T(h)$ from eq. (12) into the left hand side of eq. (14) gives x_{CH_4} of the saturated $\text{CH}_4 + \text{N}_2$ mixture as function of the altitude h . The corresponding mole fraction y_{CH_4} is calculated by

$$y_{\text{CH}_4} = \frac{x_{\text{CH}_4} \cdot \gamma_{\text{CH}_4} \cdot p_{\text{CH}_4}^{\text{sat}}(T(h)) \cdot \pi_{\text{CH}_4}}{p(h)} \quad (15)$$

where $p(h)$ is eq. (14).

Results are shown in Fig. 3 which also shows the temperature profile (eq. (12)) and the solid-liquid equilibrium of methane. Fig. 3 demonstrates that only values of y_{CH_4} below the $y_{\text{CH}_4}(h)$ curve represent a dry atmosphere. For $y_{\text{CH}_4} > y_{\text{CH}_4}(h)$ phase splitting, i. e. condensation occurs, e. g. for $y = 0.049$ above 8700 m or for $y = 0.036$ above 12000 km. These are the cloud heights where we also can expect rain fall provided there is no supersaturation. Fig. 3 also shows that "methane snow" will never occur in Titan's atmosphere since the solid-liquid line of CH_4 does not intersect the $x_{\text{CH}_4}(h)$ curve above the temperature minimum of 73 K (s. Fig. 2) due to freezing point depression of the $\text{CH}_4 + \text{N}_2$ mixture. $y_{\text{CH}_4} = 0.0975$ and $x_{\text{CH}_4} = 0.834$ are the saturation values at the bottom as already calculated for the real model in section 3.

5. Approximative scenario of Titan's atmosphere in the past and in the future

To our knowledge no attempts have been made so far to develop a thermodynamically consistent procedure of a time dependent scenario of Titan's atmosphere.

The simplified scenario presented here is based on the assumption that the gaseous atmosphere as well as the liquid reservoirs on Titan's surface consist of binary $\text{CH}_4 + \text{N}_2$ mixtures which behave as ideal gases in the vapor phase and obey Raoult's ideal law. Further we assume that the total amount of N_2 remains unchanged over the time, only CH_4 underlies a photochemical destruction process occurring exclusively in the gaseous phase, i. e. in the atmosphere, with a known destruction rate constant. The photokinetic process is assumed to be slow compared to the rate for establishing the thermodynamic phase equilibrium. Starting with the mole numbers of $\text{CH}_4, n_{\text{CH}_4}^g$ and $\text{N}_2, n_{\text{N}_2}^g$ in the atmospheric (gaseous) phase given by the force balances between gravitational forces and pressure forces at $h = 0$

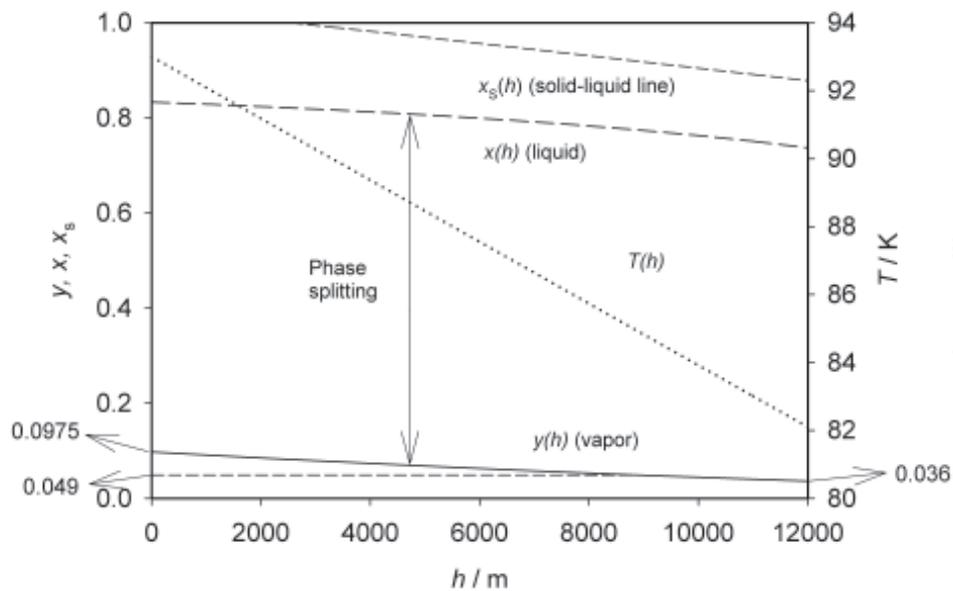


Fig. 3. Composition profile in a polytropic atmosphere (see text)

$$n_{\text{CH}_4}^g = \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} x_{\text{CH}_4} \quad \text{and} \quad n_{\text{N}_2}^g = \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} (1 - x_{\text{CH}_4}) \quad (16)$$

the total mole fraction of methane \bar{x}_{CH_4} being an averaged value of **both** phases is

$$\bar{x}_{\text{CH}_4} = \frac{n_{\text{CH}_4}^l + x_{\text{CH}_4} \cdot \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g}}{n_{\text{CH}_4}^l + x_{\text{CH}_4} \cdot \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} + n_{\text{N}_2}^l + (1 - x_{\text{CH}_4}) \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g}} \quad (17)$$

where $n_{\text{CH}_4}^l$ and $n_{\text{N}_2}^l$ are the mole numbers of CH_4 and N_2 in the liquid phase respectively. A is the surface area of Titan (s. Table 1).

Since the total mole number of N_2 , $n_{\text{N}_2}^{\text{tot}}$, is given by

$$n_{\text{N}_2}^{\text{tot}} = n_{\text{N}_2}^l + n_{\text{N}_2}^g = (1 - x_{\text{CH}_4})(n_{\text{N}_2}^l + n_{\text{CH}_4}^l) + (1 - x_{\text{CH}_4}) \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} \quad (18)$$

the sum of mole numbers of CH_4 and N_2 in the liquid phase is

$$n_{\text{N}_2}^l + n_{\text{CH}_4}^l = \frac{n_{\text{N}_2}^{\text{tot}}}{1 - x_{\text{CH}_4}} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g}$$

With $x_{\text{CH}_4} = n_{\text{CH}_4}^l / (n_{\text{CH}_4}^l + n_{\text{N}_2}^l)$ eq. (17) can now be rewritten as

$$\bar{x}_{\text{CH}_4} = \frac{x_{\text{CH}_4} \left[\frac{n_{\text{N}_2}^{\text{tot}}}{1 - x_{\text{CH}_4}} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} + \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} \right]}{x_{\text{CH}_4} \left[\frac{n_{\text{N}_2}^{\text{tot}}}{1 - x_{\text{CH}_4}} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} + \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} \right] + n_{\text{N}_2}^{\text{tot}}} \quad (19)$$

\bar{x}_{CH_4} in eq. (19) depends on time through x_{CH_4} , the mole fraction of CH_4 in the liquid phase, all other parameters $p_{\text{CH}_4}^{\text{sat}}, p_{\text{N}_2}^{\text{sat}}, M_{\text{N}_2}, M_{\text{CH}_4}, g$ and in particular $n_{\text{N}_2}^{\text{tot}}$ are constant, i. e. they do not depend on time provided the temperature is also independent on time.

Below the wavelength $\lambda = 1650 \text{ \AA}$ methane dissociates according to the reaction scheme presented in the introductory section with the destruction rate of $4 \cdot 10^{-12} \text{ kg m}^{-2} \text{ s}^{-1} = 2.5 \cdot 10^{-10} \text{ mol m}^{-2} \cdot \text{s}^{-1}$ (Lorenz et al., 1997; Yung & DeMore, 1999). The total destruction rate on Titan is therefore $2.5 \cdot 10^{-10} \cdot 4\pi R_T^2 = 2.1 \cdot 10^4 \text{ mol} \cdot \text{s}^{-1}$. The loss of CH_4 is proportional to the sunlight intensity I_S and the mole number of CH_4 in the atmosphere $n_{\text{CH}_4}^g$ (see eq. (16)).

$$\begin{aligned} \frac{dn_{\text{CH}_4}^t}{dt} &= 2.1 \cdot 10^4 = -n_{\text{CH}_4}^g \cdot I_S \cdot k' \\ &= -k \cdot x_{\text{CH}_4}(t) \cdot p_{\text{CH}_4}^{\text{sat}} \cdot A / (M_{\text{CH}_4} \cdot g) \text{ mol} \cdot \text{s}^{-1} \end{aligned} \quad (20)$$

with $I_S \cdot k' = k$ where $x_{\text{CH}_4}(t)$ is the mole fraction of CH_4 in the liquid phase at time t . From eq. (2) $x_{\text{CH}_4}(t=0) = 0.698$ is the mole fraction of CH_4 in the liquid phase at present, and it follows:

$$k = \frac{2.1 \cdot 10^4 \cdot M_{\text{CH}_4} \cdot g}{0.698 \cdot p_{\text{CH}_4}^{\text{sat}} \cdot A}$$

We now have to integrate eq. (20):

$$\int_0^t \frac{dn_{\text{CH}_4}^{\text{tot}}}{x_{\text{CH}_4}(t)} = -K \cdot t \quad (21)$$

with

$$K = k \cdot \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} = 2.1 \cdot 10^4 / 0.698 = 3.0 \cdot 10^4 \text{ mol} \cdot \text{s}^{-1}$$

where the time t can be positive (future) or negative (past). Eq. (21) with $K = \text{const}$ implies that the luminosity of the sun has been constant all the time, which is a realistic assumption with exception of the early time of the solar system Yung & DeMore (1999).

To solve the integral in eq. (21) we write:

$$dn_{\text{CH}_4}^{\text{tot}} = \left(\frac{dn_{\text{CH}_4}^{\text{tot}}}{d\bar{x}} \right) \cdot \left(\frac{d\bar{x}}{dx_{\text{CH}_4}} \right) dx_{\text{CH}_4} \quad (22)$$

Considering that $n_{\text{N}_2}^{\text{tot}} = \text{const}$ we obtain with $\bar{x} = n_{\text{CH}_4}^{\text{tot}} / (n_{\text{CH}_4}^{\text{tot}} + n_{\text{N}_2}^{\text{tot}})$:

$$\frac{dn_{\text{CH}_4}^{\text{tot}}}{d\bar{x}} = \frac{(n_{\text{CH}_4}^{\text{tot}} + n_{\text{N}_2}^{\text{tot}})^2}{n_{\text{N}_2}^{\text{tot}}} \quad (23)$$

and from differentiating eq. (19):

$$\frac{d\bar{x}_{\text{CH}_4}}{dx_{\text{CH}_4}} = \frac{n_{\text{N}_2}^{\text{tot}} \left(\frac{n_{\text{N}_2}^{\text{tot}}}{(1-x_{\text{CH}_4})^2} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} + \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} \right)}{\left[x_{\text{CH}_4} \left(\frac{n_{\text{N}_2}^{\text{tot}}}{1-x_{\text{CH}_4}} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} + \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} \right) + n_{\text{N}_2}^{\text{tot}} \right]^2} \quad (24)$$

Since the denominator of eq. (24) is equal to $(n_{\text{N}_2}^{\text{tot}} + n_{\text{CH}_4}^{\text{tot}})^2$ substituting eq. (23) and eq. (24) into eq. (22) and then in eq. (21) gives:

$$-Kt = \int_{x_{\text{CH}_4}(t=0)}^{x_{\text{CH}_4}(t)} \left(\frac{n_{\text{N}_2}^{\text{tot}}}{(1-x_{\text{CH}_4})^2} - \frac{p_{\text{N}_2}^{\text{sat}} \cdot A}{M_{\text{N}_2} \cdot g} + \frac{p_{\text{CH}_4}^{\text{sat}} \cdot A}{M_{\text{CH}_4} \cdot g} \right) \cdot \frac{dx_{\text{CH}_4}}{x_{\text{CH}_4}} \quad (25)$$

The integral in eq. (25) can be solved analytically and the result is:

$$\begin{aligned} -Kt = & n_{\text{N}_2}^{\text{tot}} \left[\frac{1}{1-x_{\text{CH}_4}(t)} - \frac{1}{1-x_{\text{CH}_4}(t=0)} \right. \\ & \left. - \ln \left(\frac{1-x_{\text{CH}_4}(t)}{1-x_{\text{CH}_4}(t=0)} \cdot \frac{x_{\text{CH}_4}(t=0)}{x_{\text{CH}_4}(t)} \right) \right] + \frac{A}{g} \left(\frac{p_{\text{CH}_4}^{\text{sat}}}{M_{\text{CH}_4}} - \frac{p_{\text{N}_2}^{\text{sat}}}{M_{\text{N}_2}} \right) \\ & \cdot \ln \left(\frac{x_{\text{CH}_4}(t)}{x_{\text{CH}_4}(t=0)} \right) \end{aligned} \quad (26)$$

Eq. (19) and eq. (26) are the basis for discussing the scenario.

The pressure of the $\text{CH}_4 + \text{N}_2$ mixture is given by

$$p(x_{\text{CH}_4}) = x_{\text{CH}_4} (p_{\text{CH}_4}^{\text{sat}} - p_{\text{N}_2}^{\text{sat}}) + p_{\text{N}_2}^{\text{sat}} \quad (27)$$

or

$$p(y_{\text{CH}_4}) = \frac{y_{\text{CH}_4} \cdot p_{\text{N}_2}^{\text{sat}}}{p_{\text{CH}_4}^{\text{sat}} + y_{\text{CH}_4} (p_{\text{N}_2}^{\text{sat}} - p_{\text{CH}_4}^{\text{sat}})} \cdot (p_{\text{CH}_4}^{\text{sat}} - p_{\text{N}_2}^{\text{sat}}) + p_{\text{N}_2}^{\text{sat}} \quad (28)$$

where $p(x_{\text{CH}_4}) = p(y_{\text{CH}_4})$ is the total pressure as function of x_{CH_4} or y_{CH_4} respectively.

In Fig. 4 $p(x_{\text{CH}_4})$, $p(y_{\text{CH}_4})$ and $p(\bar{x}_{\text{CH}_4})$ with \bar{x}_{CH_4} taken from eq. (19) are plotted in a common diagram at 93 K. Three different values of $n_{\text{N}_2}^{\text{tot}}$ have been chosen for calculating $p(\bar{x}_{\text{CH}_4})$: $n_{\text{N}_2}^{\text{tot}} = 3.08 \cdot 10^{20}$ mol corresponds to a surface of Titan which is covered by 4 % of lakes with a depth of 100 m, $n_{\text{N}_2}^{\text{tot}} = 3.39 \cdot 10^{20}$ mol has the same coverage but a depth of 1000 m. $n_{\text{N}_2}^{\text{tot}} = 10.16 \cdot 10^{20}$ mol corresponds to a coverage of 28 percent and a depth of 600 m. This is exactly the value where $n_{\text{N}_2}^{\text{g}} = n_{\text{N}_2}^{\text{tot}}$ when x_{CH_4} becomes zero according to eq. (16).

Fig. 4 illustrates the "lever rule" of binary phase diagrams. For the present situation with $y_{\text{CH}_4} = 0.074$ and $x_{\text{CH}_4} = 0.698$ the dashed horizontal line indicates the 2-phase region with \bar{x}_{CH_4} -values corresponding to their $n_{\text{N}_2}^{\text{tot}}$ -values. The higher $n_{\text{N}_2}^{\text{tot}}$ is the closer is \bar{x}_{CH_4} to the value of x_{CH_4} . The \bar{x}_{CH_4} -trajectories indicated by arrows show how \bar{x}_{CH_4} is changed with decreasing values of x_{CH_4} , i. e. with increasing time. It is interesting to note that the trajectories with $n_{\text{N}_2}^{\text{tot}} = 3.03 \cdot 10^{20}$ mol and $n_{\text{N}_2}^{\text{tot}} = 3.39 \cdot 10^{20}$ mol end on the $p(y_{\text{CH}_4})$ -curve. This means that after a certain time \bar{x}_{CH_4} becomes equal to y_{CH_4} , and all liquid reservoirs on Titan would have disappeared. The surface has dried out and methane being now exclusively present in the atmosphere will be photochemically destructed according to a first order kinetics. Finally a dry atmosphere containing pure N_2 will survive. In case of $n_{\text{N}_2}^{\text{tot}} = 10.16 \cdot 10^{20}$ mol the trajectory ends at $y_{\text{CH}_4} = \bar{x}_{\text{CH}_4} = x_{\text{CH}_4} = 0$ and at $p = p_{\text{N}_2}^{\text{sat}}$ which means that the atmosphere consist of pure N_2 . For $n_{\text{N}_2}^{\text{tot}} > 10.16 \cdot 10^{20}$ mol the final situation

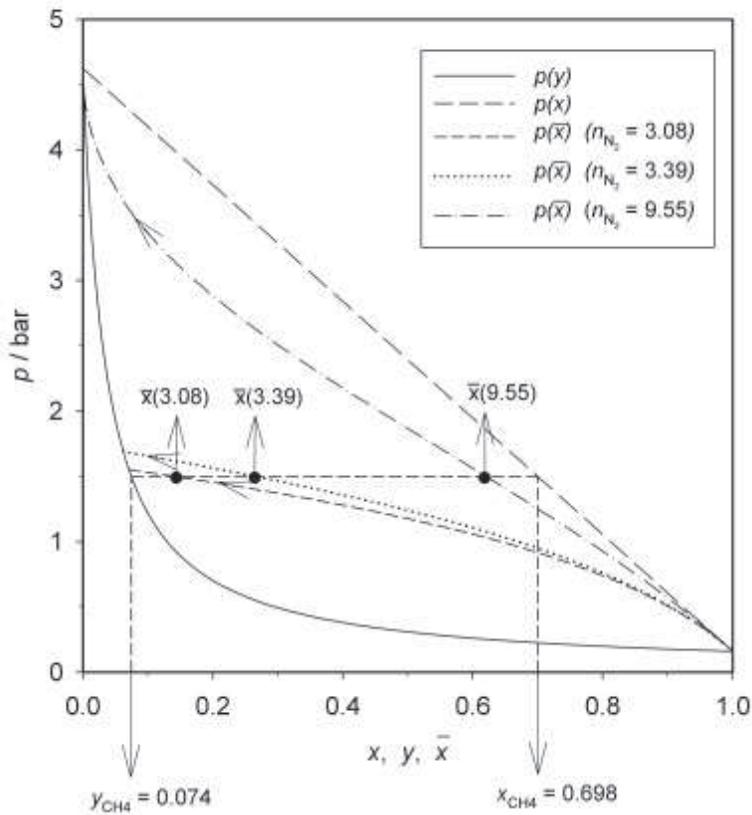


Fig. 4. Equilibrium x, g diagram of an ideal binary $N_2 + CH_4$ mixture with trajectories of the total molefraction of CH_4 \bar{x} at different total mole numbers of N_2 $n_{N_2}^{tot}$

will be an atmosphere of pure N_2 with $p = p_{sat}^{N_2}$ and liquid reservoirs with pure N_2 on the surface.

The explicit time evolution of x_{CH_4} obtained by eq. (26) is shown in Fig. 5 and Fig. 6. According to these results $x_{CH_4} > 0.9$ can be expected at the time of Titan's formation ($4 \cdot 10^9$ years ago) for all values of $n_{N_2}^{tot}$ considered here.

According to Fig. 5 the lakes will have disappeared in $10 \cdot 10^6$ years ($n_{N_2}^{tot} = 3.08 \cdot 10^{20}$ mol) or in $23 \cdot 10^6$ years ($n_{N_2}^{tot} = 3.39 \cdot 10^{20}$ mol) with the "last drop" of a liquid composition $x_{CH_4} \approx 0.685$ or 0.655 respectively. At higher values of $n_{N_2}^{tot}$ the liquid mixtures phase would exist much longer since $n_{CH_4}^{tot}$ is also larger at the same composition. In case of $n_{N_2}^{tot} = 10.16 \cdot 10^{20}$ mol and $n_{N_2}^{tot} = 25 \cdot 10^{20}$ mol (see Fig. 6) CH_4 would have disappeared at Titan in ca. $350 \cdot 10^6$ years and $2.0 \cdot 10^9$ years respectively resulting in a pure N_2 -atmosphere with liquid N_2 reservoirs ($n_{N_2}^{tot} > 10 \cdot 16 \cdot 10^{20}$ mol).

Fig. 7 shows the change of the total amount of CH_4 $n_{CH_4}^{tot} = n_{CH_4}^g + n_{CH_4}^l$ on Titan as function of time for the past and the future also based on the present values of $x_{CH_4} = 0.658$ and $y_{CH_4} = 0.074$ for different values of $n_{N_2}^{tot}$ as indicated. $n_{CH_4}^{tot}$ has been calculated by

$$n_{CH_4}^{tot}(t) = \frac{\bar{x}_{CH_4}(t)}{1 - \bar{x}_{CH_4}(t)} \cdot n_{N_2}^{tot}$$

with $\bar{x}_{CH_4} = \bar{x}_{CH_4}(x_{CH_4}(t))$ using eq. (19) with $x_{CH_4}(t)$ from eq. (26). According to the model

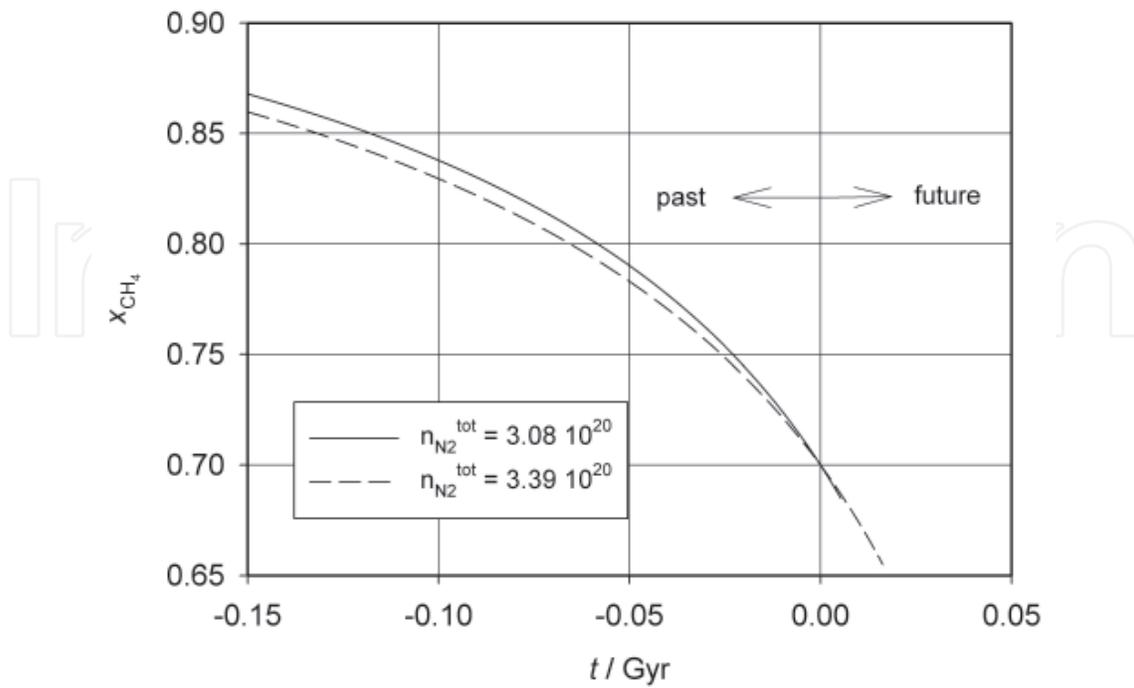


Fig. 5. Molefraction x_{CH_4} in the liquid phase as function of time at fixed total mole numbers of N_2 on Titan's surface $n_{\text{N}_2}^{\text{tot}} = 3.08 \cdot 10^{20}$ mol and $n_{\text{N}_2}^{\text{tot}} = 3.39 \cdot 10^{20}$ mol.

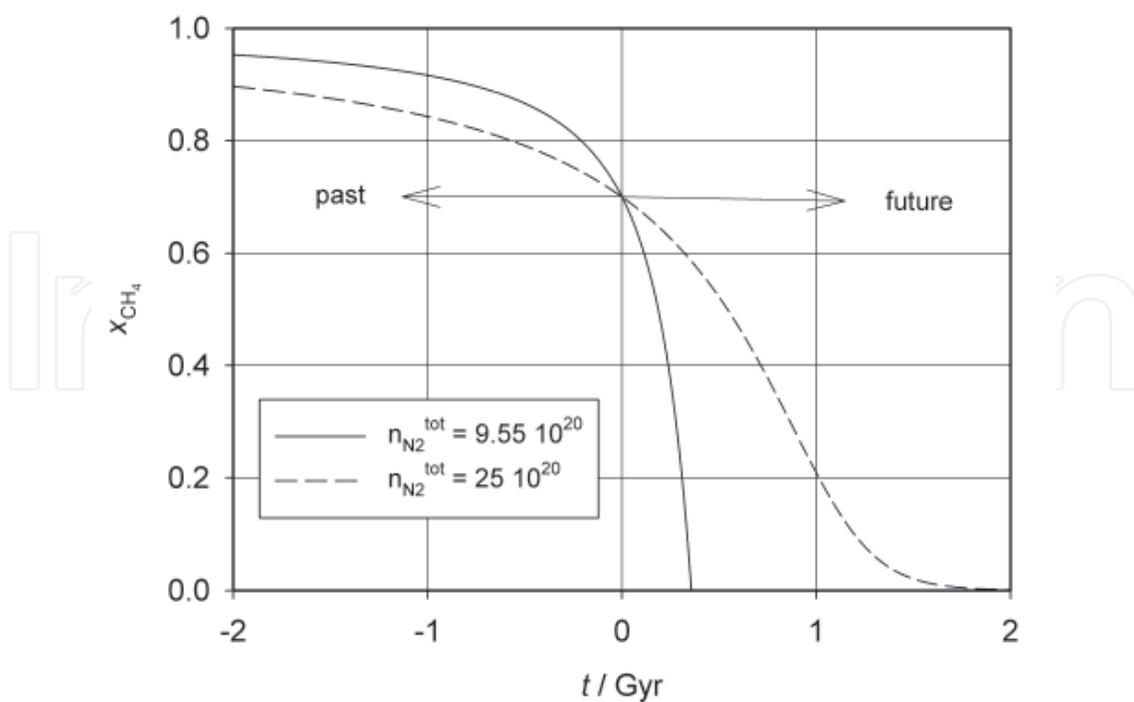


Fig. 6. Molefraction x_{CH_4} in the liquid phase as function of time at fixed total mole numbers of N_2 on Titan's surface: $n_{\text{N}_2}^{\text{tot}} = 9.55 \cdot 10^{20}$ mol and $n_{\text{N}_2}^{\text{tot}} = 25 \cdot 10^{20}$ mol.

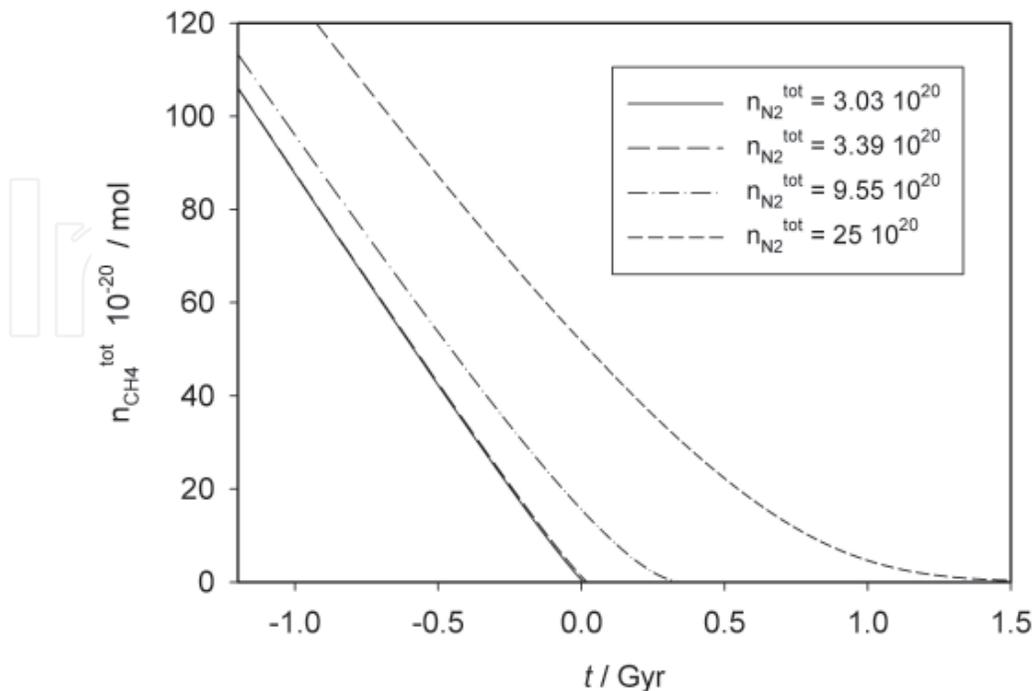


Fig. 7. Total mole number of CH₄ on Titan's surface as function of time at fixed total model numbers of N₂ as indicated

much more methane must have existed on Titan in the past than today, i. e., Titan has possibly been covered by a deep liquid ocean consisting of a N₂ + CH₄ mixture with distinctly higher concentrations of methane than today. It might also be possible that the amount of CH₄ and N₂ is already much higher at present than the detectable lakes on Titan's surface suggest due to hidden reservoirs such as "humidity" in micropores of Titan's icy crust.

The calculations of this simple scenario show that the fate of Titan's atmosphere and lakes sensitively depends on the amount and on the composition of liquid present today on Titan's surface. As long as there are no certain values available neither the future nor the past can be predicted with acceptable reliability. If this situation is changed the model of the scenario can be extended to real ternary mixture also including ethane. At this point the purpose of this section was to demonstrate how scenario calculations can be performed.

6. Titan's internal structure

As already mentioned the low density indicates that Titan's interior must contain considerable amounts of water beside rocky material. Assuming that these different chemical components are well separated we expect that Titan has an inner core consisting of rock, i. e. silicates, with an averaged density $\rho_{\text{Rock}} = 3 \text{ g} \cdot \text{cm}^{-3}$, the mantle and the crust will mainly consist of liquid water and ice with an averaged density $\rho_{\text{H}_2\text{O}} = 1.1 \text{ g} \cdot \text{cm}^{-3}$. Accepting these figures we are able to determine roughly the amount of water in the outer shell as well as the amount of silicate in the core. We also can calculate the central pressure and the pressure as function of radius r with $r = 0$ at the center. First the radius r_1 of transition from the rocky material to the water phase is determined from the following mass balance:

$$m_{\text{H}_2\text{O}} + m_{\text{Rock}} = \frac{4}{3}\pi \langle \rho \rangle \cdot R_T^3 = \frac{4}{3}\pi \rho_{\text{H}_2\text{O}} [R_T^3 - r_1^3] + \frac{4}{3}\pi \rho_{\text{Rock}} \cdot r_1^3 \quad (29)$$

where R_T is Titan's radius (see Table 1).

Solving eq. (29) for r_1^3 gives:

$$r_1^3 = R_T^3 \frac{\langle \rho \rangle - \rho_{\text{H}_2\text{O}}}{\rho_{\text{Rock}} - \rho_{\text{H}_2\text{O}}} \quad (30)$$

Using the known data of $\langle \rho \rangle = 1.88 \text{ g} \cdot \text{cm}^{-3}$ (s. Table 1), $\rho_{\text{H}_2\text{O}}$, ρ_{Rock} , and R_T the result is

$$r_1 = 1913 \text{ km} \quad \text{or} \quad r_1/R_T = 0.743$$

This is a rough estimate because $\rho_{\text{H}_2\text{O}}$ and ρ_{Rock} are averaged values over the pressure and temperature profile of Titan's interior. Improved results can be obtained by considering compressibilities and thermal expansion coefficients if these profiles would be known.

The mass fraction $w_{\text{H}_2\text{O}}$ of H_2O in Titan is:

$$w_{\text{H}_2\text{O}} = \rho_{\text{H}_2\text{O}} (R_T^3 - r_1^3) / [\rho_{\text{H}_2\text{O}} (R_T^3 - r_1^3) + \rho_{\text{Rock}} \cdot r_1^3] = 0.345$$

and the corresponding mass fraction of rock is $w_{\text{Rock}} = 1 - w_{\text{H}_2\text{O}} = 0.655$.

Using the hydrostatic equilibrium condition

$$dp = -\rho \cdot g \cdot dr \quad (31)$$

the pressure profile of Titan's interior can easily be calculated. Using the local gravity acceleration $g(r)$

$$g(r) = G \cdot \frac{m(r)}{r^2} = \frac{4}{3}\pi G \cdot \rho(r)$$

eq. (31) can be written:

$$dp = -G\rho^2(r) \cdot \frac{4}{3}\pi r \cdot dr \quad (32)$$

with the gravitational constant $G = 6.673 \cdot 10^{-11} [\text{J} \cdot \text{m} \cdot \text{kg}^{-2}]$ and ρ either $\rho_{\text{H}_2\text{O}}$ or ρ_{Rock} . Integration of eq. (32) gives the central pressure p_0 assuming that $\rho_{\text{H}_2\text{O}}$ and ρ_{Rock} are independent of the pressure p with $p(r = R_T) \approx 0$:

$$\begin{aligned} p_0 &= \frac{2}{3}\pi G [\rho_{\text{H}_2\text{O}}^2 (1 - (0.743)^2) + \rho_{\text{Rock}} \cdot (0.743)^2] \cdot R_T^2 = 5.106 \cdot 10^9 \text{ Pa} \\ &= 51 \text{ kbar} \end{aligned} \quad (33)$$

where $r_1/R_T = 0.743$ has been used.

The pressure p_1 at r_1 is:

$$p_1 = p_0 - \rho_{\text{Rock}}^2 \cdot \frac{2}{3}G \cdot r_1^2 = 0.502 \cdot 10^9 \text{ Pa} \cong 5 \text{ kbar} \quad (34)$$

The dependence of the pressure p on r is given by:

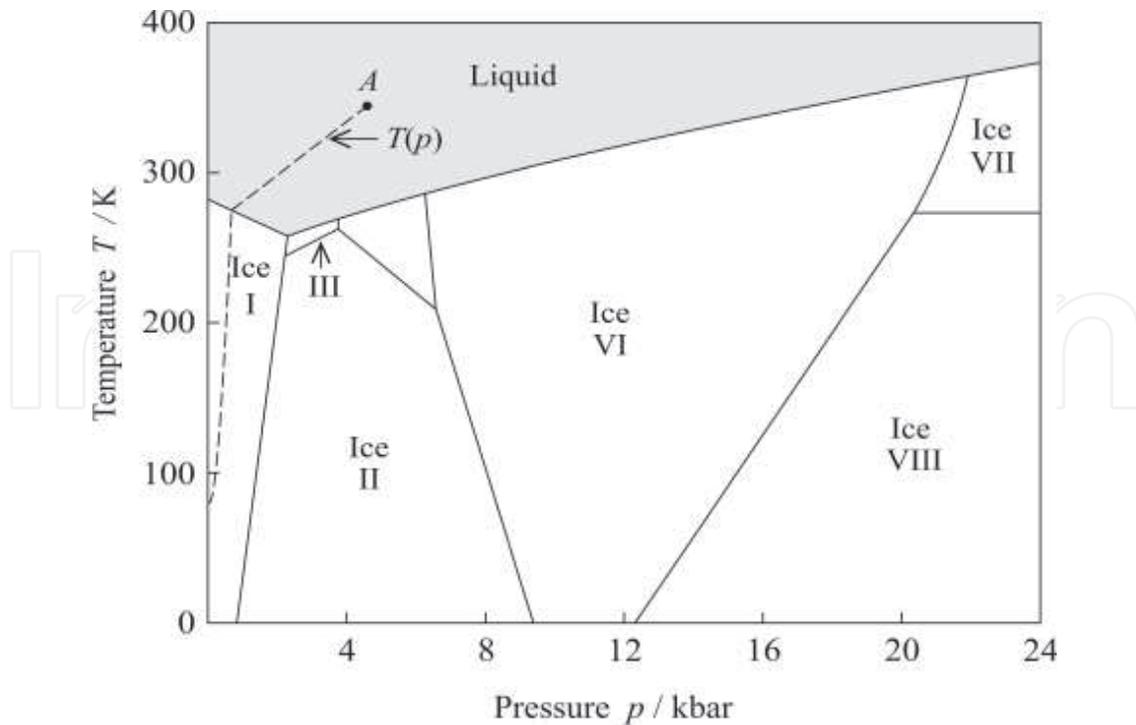


Fig. 8. Phase diagram of water. - - - - estimated $T(p)$ curve inside Titan. A = assumed transition point from aqueous phase to the rocky material

$$\begin{aligned}
 p(r) &= p_0 - \rho_{\text{Rock}}^2 \cdot \frac{2}{3} \pi G \cdot r^2 && (\text{for } r \leq 0.743 R_T) \\
 p(r) &= p_0 + \left[(\rho_{\text{H}_2\text{O}}^2 - \rho_{\text{Rock}}^2) \cdot (0.743 \cdot R_T)^2 - \rho_{\text{H}_2\text{O}}^2 \cdot r^2 \right] \frac{2}{3} \pi G && (\text{for } r \geq 0.743 \cdot R_T)
 \end{aligned}
 \tag{35}$$

The upper layer of the aqueous system is the crust consisting of water ice up to a depth of ca. 200 km followed by a layer of liquid water up to the depth where the solid phase of rocky materials begins. The existence of solid and liquid water layers can be understood by inspecting the phase diagram of water shown in Fig. 8.

Figure 8 shows that the tentative $T(p)$ curve most probably intersects the solid-liquid equilibrium line of water at ca. 0.5 kbar and $r = 2300$ km. In the literature (Lunine & Stevenson, 1987) there are also aqueous NH_3 solutions discussed instead of pure water leading to a second solid phase of pure water which is likely to exist between $r = 2100$ km and $r = 1913$ km. The dependence of pressure p on r calculated according to eq. (35) is shown in Fig. 9.

7. Conclusions

- Using thermodynamic methods and comparatively simple theoretical tools the composition of liquid lakes on Titan's surface can be predicted being in acceptable agreement with the known atmospheric composition.

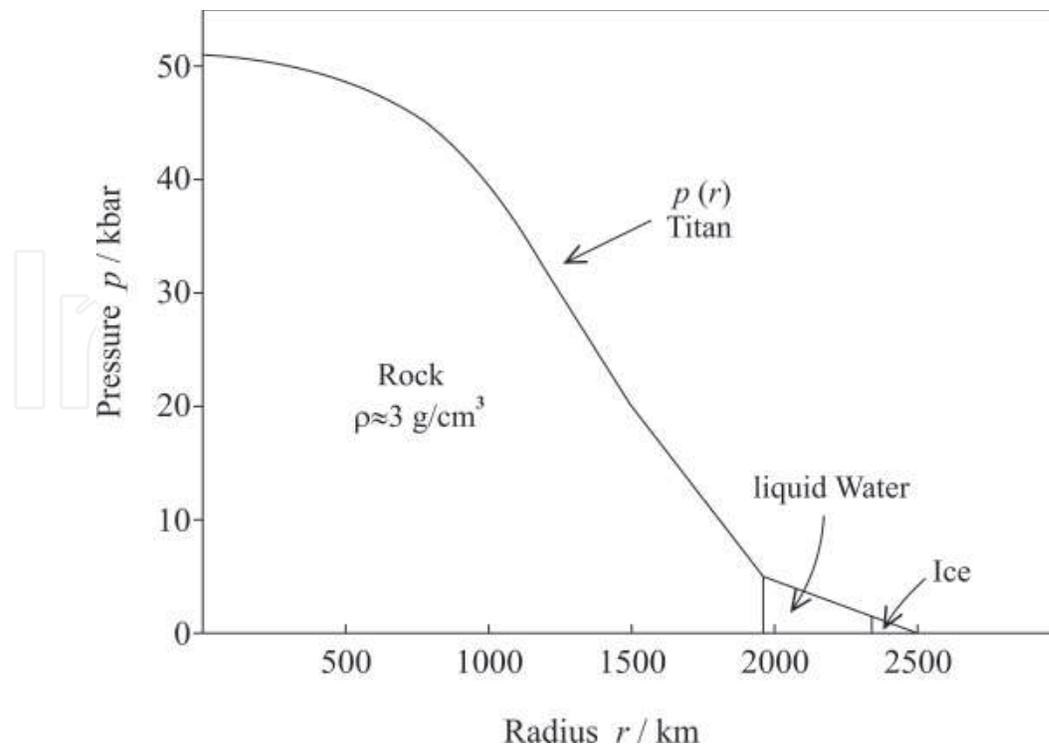


Fig. 9. Pressure as function of the distance r from Titan's center

- The cloud ceiling of $\text{CH}_4 + \text{N}_2$ mixtures in the troposphere can be estimated. Depending on the degree of saturation on the bottom altitudes between 8 and 12 km are predicted provided the vapor is not supersaturated. In the model calculations presented here a real mixture without ethane has been treated.
- A rough estimation of atmospheric scenarios in the past and the future can be made. The results depend essentially on the total amount of liquid on Titan's surface present today.
- An imagination of the internal structure of Titan can be provided predicting an aqueous mantle of ca. 700 km thickness and a hard core consisting of rocky material with a central pressure of ca. 51 kbar.

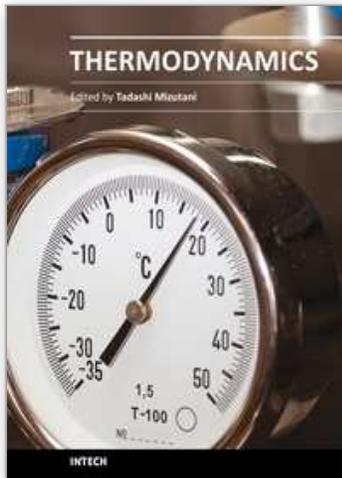
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