

UPPER LIMIT OF HYDROGEN AND HELIUM CONCENTRATIONS ON TITAN

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Abstract. The satellite Titan is commonly quoted as possessing an atmosphere consisting of at least 2×10^4 cm atm of methane. Plausible additional atmospheric constituents like hydrogen and helium are assumed to have completely escaped from the satellite. However, the employment of recent techniques to the upper atmosphere of Titan permits an improved estimate of the upper limits of the hydrogen to methane and helium to methane mixing ratios existing in the lower atmosphere of Titan, namely $10^{-6 \pm 1}$ and $10^{-3.5 \pm 0.5}$.

1. Introduction

Of the 32 identified satellites in the solar system, only Titan, a satellite of Saturn, is commonly accepted as possessing an atmosphere. Kuiper (1952), in evaluating the spectra of Titan, particularly at 6190 Å, concluded that the atmosphere of Titan consisted of at least 2×10^4 cm atm of CH₄. Proceeding from this information, Kuiper (1952), using an approximation method for computing the exospheric temperature in conjunction with a simplified escape criterion, deduced that all molecules with molecular weights less than 10 must have escaped from Titan. However, since this original study, our knowledge of the physical mechanisms controlling the temperature and density structure of the upper atmosphere of a planetary body has increased significantly. Therefore, a re-examination of the upper atmosphere of Titan, using procedures similar to those suggested by Chamberlain (1962) could result in improved estimates of several physical parameters associated with the atmosphere of Titan, in particular the maximum atmospheric hydrogen concentration.

Spectroscopically, only CH₄ has been positively identified on Titan. Ammonia, due to its low frost point, has probably precipitated out; hence it is not surprising that an analysis of the 6450 Å band of NH₃ by Kuiper (1952) resulted in an ammonia upper limit of only 3×10^2 cm atm.

Plausible additional atmospheric constituents are hydrogen and helium; nevertheless, on account of their low molecular weights, both gases have a strong tendency to dissipate rapidly through gravitational escape. Specifically, the escape rate is a function of both the height and temperature of the exosphere. However, both parameters are in turn dependent upon the relative concentrations of these same gases; this is particularly true for hydrogen. Under such circumstances, as the quantity of these gases decreases, the remaining portions become less susceptible to escape, until a threshold level is reached below which equilibrium concentrations can be expected to be maintained through either outgassing and/or photolysis. The purpose of this

article is to determine these threshold levels for H_2 and He through a study of the upper atmosphere of Titan.

2. Upper Atmosphere Composition

The composition of the upper atmosphere depends to a large extent upon the photochemistry associated with methane; however, studies of the problem with particular reference to Jupiter have not produced uniform results. Wildt (1937) noted that the absorption spectrum of complex hydrocarbons extends beyond that of CH_4 , also that of all the hydrocarbons only CH_4 appears to be stable in the presence of atomic hydrogen. He concluded that, in the presence of sufficient H_2 , the formation of C_2H_6 will be almost completely suppressed. In this situation, the photochemical decomposition of CH_4 will be thwarted, and only small amounts of molecules formed as a result of the photochemical processes should be expected. In contrast, Cadle (1962) indicated that when CH_4 undergoes appreciable photolysis its concentration approaches zero and that the vast majority of the carbon from the dissociated methane reappears as ethane (C_2H_6). In a recent numerical study, Strobel (1969a), noting the numerous laboratory studies concerning the photolysis of CH_4 since the article by Cadle, concluded that in the Jovian atmosphere the over-all mixing ratio of ethane to methane was approximately 10^{-4} . Applying this technique to Titan resulted in a similar conclusion, namely, that the ethane-methane mixing ratio is small, approximately 10^{-5} (Strobel, 1969b).

We are therefore presented with two extreme views concerning the photolysis of methane: complete dissociation and, in effect, no dissociation. In the initial series of models in this article, CH_4 will be assumed to be completely dissociated and converted to ethane in the upper atmosphere of Titan. This assumption is based not so much on the probable composition resulting from the photolysis of CH_4 , but on the fact that C_2H_6 at 12.2μ , especially at low temperatures is superior to CH_4 at 7.7μ as a cooling agent for Titan. This model will therefore produce minimum exospheric temperatures for a given H_2 concentration, and, in essence, an estimate of the upper limit of H_2 on Titan independent of the present uncertainties associated with the photochemistry of methane. Consequently, above the mesopause, cooling was limited to this single vibrational energy exchange, since pure rotational exchanges will be of minor importance for molecules with a center of symmetry like CH_4 , C_2H_2 , C_2H_6 , C_3H_8 , and H_2 (Goody, 1964). Therefore, on Titan in this initial series, equilibrium conditions will consist of a CH_4 -dominated lower atmosphere associated with a small amount of free hydrogen. At the mesopause, a mixture of mainly C_2H_6 , CH_4 , and molecular and/or atomic hydrogen is assumed to prevail, with cooling restricted to C_2H_6 . Above the mesopause, atomic hydrogen is produced from molecular hydrogen by dissociative recombination following the ionization of molecular hydrogen. Through 3-body recombination, molecular hydrogen is reformed at lower altitudes. Based upon these processes, Zabriskie (1960) has concluded that, in the vicinity of the Jovian lower thermosphere, hydrogen is predominantly in the molecular form ($H/H_2 \sim 10^{-3}$). The photochemical analysis by Strobel indicates that, in the region of the Jovian

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mesopause, molecular hydrogen likewise predominates ($H/H_2 \lesssim 10^{-6}$). Applying these methods to Titan resulted in the conclusion that in the lower thermosphere, for hydrogen to methane mixing ratios in excess of 10^{-3} , the H to H_2 ratio is less than one, but, through diffusion, atomic hydrogen will become the dominant constituent in the upper thermosphere and exosphere of Titan. For mixing ratios less than 10^{-3} atomic hydrogen dominates over molecular hydrogen throughout the entire upper atmosphere. The specific mesopause H/H_2 mixing ratios adopted are found in Tables I and II. Above the mesopause, under normal conditions, the constituents are assumed to be in diffusive equilibrium, while below the mesopause mixing dominates.

3. Models and Results

In reconstructing the temperature and density structure of the upper atmosphere, the heat conduction equation, the hydrostatic equation, the cooling term, and the assumptions associated with these equations as well as the procedure for applying these equations are similar to those outlined by McGovern (1969), with the following exceptions: (1) selection of a higher heating efficiency (0.30); (2) higher cooling rate by C_2H_6 at low temperatures by reducing the cooling constant x_i from 0.95 to 0.75; so that the relative variation in the cooling as a function of temperature is similar to that for CO_2 ; (3) maximum solar flux limited to the wavelength interval between 31 and 964 Å; (4) selected a mesopause height and temperature of 200 km and 80 K, respectively; (5) computed average day side instead of sub-solar point temperature; and (6) physical parameters pertinent to Titan, for example, solar flux and gravity, were incorporated.

The results of this numerical program for various hydrogen to ethane mixing ratios at the mesopause are tabulated in Table I. The percentage of hydrogen in the atomic state at the mesopause is listed in column 2, the remaining portion is H_2 .

For the particular range of mixing ratios selected, the mesopause density (10^{11} to 10^{12} molecules cm^{-3}) and the temperature of the exosphere (column 3) were found to be relatively stable. In contrast, the base of the exosphere (column 4) varies considerably, which is the primary reason for the sizable variations in the escape flux L in column 5. The escape flux (L) was computed using the following equation given by Spitzer (1949):

$$L = \pi R_e^2 n_e \bar{v} e^{-R_e/H_e} (1 + R_e/H_e),$$

where \bar{v} is the average thermal velocity, while R_e/H_e , and n_e are, respectively, the geocentric or planetocentric radius, scale height and number density of the escaping constituent at the base of the exosphere. In column 6 are the production rates of hydrogen through outgassing and/or photolysis which are necessary in order to balance the loss of hydrogen through escape.

The maximum photon flux reaching Titan capable of dissociating CH_4 is approximately 1.4×10^{10} photons $cm^{-2} sec^{-1}$ (Hinteregger *et al.*, 1965); therefore, the maximum possible escape flux through photolysis alone is approximately $10^{10} cm^{-2} sec^{-1}$.

TABLE I
Exospheric parameters associated with various mesopause hydrogen-to-ethane mixing ratios

Mesopause hydrogen-ethane mixing ratio	Percentage of mesopause hydrogen in atomic state	Exospheric temperature (K)	Base of exosphere ($n_0 \equiv 10^6 \text{ cm}^{-3}$)	Hydrogen escape flux (L) (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)	Equilibrium rate (Q) (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)	$(R_{\text{e}}/H_{\text{e}})_{\text{H}}$	Blow-off level $\times 10^9$ (km)	H	H_2
10^{-6}	100	120	500	1.4×10^9	2.0×10^9	3.1	4	4	10
10^{-5}	100	120	1400	1.5×10^{10}	3.9×10^{10}	2.3	4	4	10
10^{-4}	100	125	9400	$> 2.3 \times 10^{10}$	$> 6.0 \times 10^{11}$	< 1.5	4	4	10
10^{-3}	10	150	14000	$> 2.5 \times 10^{10}$	$> 1.2 \times 10^{12}$	< 1.5	4	4	9

Exospheric escape fluxes higher than $10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$ seem improbable, independent of the mixing ratio, because the time necessary for upward diffusion of hydrogen is such as to limit the escape rate. An estimate of the molecular diffusion time constant (τ) is given by $\tau = H^2/D$, where the scale height is represented by H and D is the molecular diffusion coefficient which can be approximated by $10^{17} H^{1/2}/n$. This results in a τ of 10^5 to 10^6 sec, and based upon a total exospheric concentration of 10^{15} atoms cm^{-2} , indicates that, under normal conditions, the maximum escape rate for atomic hydrogen is 10^{10} atoms $\text{cm}^{-2} \text{ sec}^{-1}$.

At mixing ratios higher than 10^{-5} , the upper atmosphere would appear to enter a chaotic stage in which τ may no longer be a limiting factor on the escape rate. Öpik (1963) has indicated that, when the thermal energy of translation exceeds the gravitational energy, the top portion of the atmosphere will 'blow-off', and that the escape of gases will be both extremely high and indiscriminate as to species. An equivalent manner of expressing this criterion is by noting that, when the ratio of the exospheric planetocentric distance to the exospheric scale height falls below 1.5, the kinetic energy will exceed the gravitational potential energy and 'blow-off' occurs. Column 7 indicates the value of this ratio for atomic hydrogen at the exospheric base. In columns 8 and 9 for the particular exospheric temperature found in column 3, the level at which the planetocentric distance to scale height ratio equals 1.5 is listed for atomic and molecular hydrogen. These results indicate that, when the mixing ratio approaches 10^{-4} , then the blow-off level falls below the theoretical base of the exosphere and the entire upper atmosphere would be in a chaotic state. Under such circumstances, the escape rate for hydrogen would be very high, requiring outgassing rates from Titan significantly higher than anticipated ($> 10^{11}$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$), in order to maintain equilibrium. Thus, based upon the assumption of the dominance of C_2H_6 in the upper atmosphere of Titan, it is concluded that the maximum hydrogen to methane mixing ratio in this atmosphere is in the vicinity of 10^{-5} .

The alternative model, namely, assuming that the dissociation of methane is very small, means that the net cooling in the upper atmosphere will decrease. As noted previously, CH_4 at 7.7μ and 150 K is several orders of magnitude (~ 3 or 4) less effective as a radiator than C_2H_6 at 12.2μ and 150 K; however, the cooling rates associated with CH_4 and C_2H_6 are both strongly dependent upon temperature. For example, CH_4 cooling per molecule at 250 K is comparable to the cooling rate of C_2H_6 at 150 K. This results from selecting a cooling constant (x_i) for CH_4 of 1.37. Under these circumstances, it is not surprising that the exospheric temperature for a pure CH_4 atmosphere approaches 250 K in contrast to 115 K for a pure C_2H_6 atmosphere; in fact, as seen from Table II, the permissible atmospheric hydrogen contents are so low that the exospheric temperature for these models and a pure CH_4 atmosphere are essentially the same. Another aspect of these results is that, when the mixing ratio (w) becomes equal to or less than 10^{-7} the base of the exosphere is no longer dominated by atomic hydrogen, in which case the escape flux of atomic hydrogen becomes dependent upon the hydrogen concentration at the mesopause and can be estimated by $L_H \approx 10^{16} w$ for a CH_4 -dominated atmosphere. A similar situation existed for a C_2H_6 -dominated upper atmosphere for $w \leq 10^{-6}$, then $L_H \approx 10^{15} w$. In both cases,

TABLE II
Exospheric parameters associated with various mesopause hydrogen-to-methane mixing ratios

Mesopause hydrogen-methane mixing ratio	Percentage of mesopause hydrogen in atomic state	Exospheric temperature (K)	Base of exosphere (km) ($n_e \equiv 10^6 \text{ cm}^{-3}$)	Hydrogen escape flux (L) (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)	Equilibrium rate (Q) (atoms $\text{cm}^{-2} \text{ sec}^{-1}$)
10^{-8}	100	245	1900	3.3×10^8	1.0×10^9
10^{-7}	100	245	1900	3.3×10^9	1.1×10^{10}
10^{-6}	100	250	2500	$> 3.0 \times 10^{10}$	$> 1.3 \times 10^{11}$

when w falls below 10^{-10} then the escape of hydrogen occurs through CH_4 molecule and the above simple relationships are no longer valid.

The sensitivity of these methods decreases rapidly with increasing molecular weight; for the application of Öpik's criterion to a pure helium-ethane upper atmosphere results in a maximum $\text{He}/\text{C}_2\text{H}_6$ mixing ratio between 5×10^{-2} and 10^{-2} . However, even at 10^{-2} the outgassing rate needed to maintain equilibrium with the escape is over an order of magnitude greater than the outgassing rate for the earth. Comparable outgassing rates are obtained when the mixing ratio approaches 10^{-3} for a C_2H_6 -dominated atmosphere and 10^{-4} for an upper atmosphere consisting mainly of CH_4 ; therefore, a reasonable upper limit for the helium-methane mixing ratio on Titan is $10^{-3.5 \pm 0.5}$.

4. Conclusions

Based upon the molecular diffusion time constant (τ), it was concluded that the maximum escape rate for atomic hydrogen under non-chaotic conditions was 10^{10} atoms $\text{cm}^{-2} \text{sec}^{-1}$. Contingent upon this escape flux, the upper limit on the hydrogen-methane mixing ratio on Titan was found to be 10^{-7} if the net dissociation of methane is small. In comparison, if the upper atmosphere is dominated by C_2H_6 , the mixing ratio upper limit is 10^{-5} , while a similar analysis yields a helium-methane upper limit of $10^{-3.5 \pm 0.5}$.

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