from the accounts. Military consumption of nuclear energy directly, in detonations and reactors, and indirectly, in weapons manufacture, raises questions that are at least as vital to the world as those raised by other uses of energy.

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Evolution of a Nitrogen Atmosphere on Titan

Abstract. *Photochemical calculations indicate that if NH_3 outgassed from Titan it should have been converted to a dense N_2 atmosphere during the lifetime of the satellite. A crucial step in the process involves a gas phase reaction of N_2H_4 with H. The most favorable conditions for this step would be the intermediate production of a CH_4-H_2 greenhouse capable of raising the gas temperature to 150°K. Subsequently about 20 bars of N_2 could have evolved. The pressure-induced opacity of 20 bars of N_2 should suffice to explain the recently measured 200°K surface temperature. Unlike the situation on Jupiter, NH_3 is not recycled on Titan by reactions involving N_2 or N_2H_4. This may explain the failure of recent attempts to detect NH_3 in the upper atmosphere of Titan.*

Hunten (*1*) first proposed that N_2 might be the dominant gas in the atmosphere of Titan. Ammonia may have been irreversibly converted (*1, 2*) to other nitrogen-bearing compounds such as N_2, N_2H_4, and CH_3NH_2. Recent measurements by Owen (*3*) place 30 cm-atm as the upper limit for NH_3 above the clouds on Titan.

We have investigated the photochemistry of NH_3 in the primordial Titan atmosphere and developed a model for the evolution of the atmosphere during geologic time. Our conclusion is that if NH_3 was available on Titan, a dense N_2 atmosphere of 14 to 19 bars at the present time is plausible. We have also estimated the amount of H_2 that would be present as a result of production in NH_3 photochemistry and loss by Jeans escape in the case of limiting flux.

We propose the following scenario. After cooling and solidification of Titan's surface, and once outgassing began, the atmosphere may have contained such gases as CH_4 and NH_3. These gases were photolyzed, and NH_3 was converted to other nitrogen-bearing compounds while CH_4 continued to build up in the atmosphere. Photolysis can convert some CH_4 to other species. On the basis of possible recapture by Titan of escaping hydrogen atoms, Strobel (*4*) has estimated that up to 60 percent of CH_4 may be recycled. Molecular hydrogen was also produced in the photolysis of these gases. Once the CH_4-H_2 surface pressure reached 0.1 bar, the greenhouse effect began to be important and the atmospheric temperature began to rise above the equilibrium value of 86°K. Calculations by Pollack (*5*) indicate that by the time the pressure of the CH_4-H_2 atmosphere reached 0.45 bar, the surface temperature would have been 150°K. Present-day spectroscopic observations place an upper limit on CH_4 much lower than the amount required for a greenhouse effect leading to a 150°K temperature. These observations, however, apply to CH_4 in the visible atmosphere above the clouds. The existence of a much larger CH_4 abundance below the clouds is entirely possible.

The photochemistry of NH_3 has been discussed in detail in the context of Jupiter in a recent paper by Atreya *et al.* (*6*). The photochemical scheme is shown in Fig. 1 and the relevant rate constants are given in Table 1. Photolysis of NH_3 in the range 160 to 230 nm leads to the formation of H and the radical NH_2. A fraction of NH_3 is recycled by the reaction of NH_2 with H (reaction R2). Reaction of NH_2 with itself (R3) forms hydrazine, N_2H_4. Assuming that N_2H_4 remains in the vapor phase, it undergoes photolysis in the same spectral range as NH_3 (R5) or reacts with H (R4). Both these processes produce the radical N_2H_3. Reactions of N_2H_3 with itself can lead to NH_3 (R8) or N_2H_4 and N_2 (R9). The recycling of NH_3 by the path R8, however, is insignificant compared to N_2 production by R9. The final products of this gas phase photochemistry are thus N_2 and H_2.

During the early phases of the evolution of the atmosphere, the NH_3 volume mixing ratio would have been determined by its saturation vapor pressure. The vapor pressure at 86°K is 1×10^{-6} mbar, at 100°K is 2×10^{-5} mbar, and at 120°K is 3×10^{-3} mbar. In any event, photolysis of NH_3 proceeded from the beginning, the altitude at which it predominantly occurred rising as the atmospheric temperature increased with the development of the CH_4-H_2 greenhouse. The photochemical cycle leading to N_2 may have terminated during the early history of the atmosphere with the formation of N_2H_4. For the range of N_2H_4 partial pressures prevailing during this period, N_2H_4 can condense at temperatures below 150°K. However, it is conceivable that the gas phase chemistry

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Table 1. Relevant chemical reactions and associated rate constants.

Reaction number	Reaction*	Rate constant†
R1	$NH_3 + h\nu \rightarrow NH_2(X) + H$	$J(NH_3)$
R2	$NH_2(X) + H \overset{+M}{\rightarrow} NH_3$	$k_2 = 6 \times 10^{-30}[M]/(1 + 3 \times 10^{-20}[M])$
R3	$NH_2(X) + NH_2(X) \overset{+M}{\rightarrow} N_2H_4$	$k_3 = 1 \times 10^{-10}$
R4	$N_2H_4 + H \rightarrow N_2H_3 + H_2$	$k_4 = 9.87 \times 10^{-12} \exp(-1198/T)$
R5	$N_2H_4 + h\nu \rightarrow N_2H_3 + H$	$J(N_2H_4)$
R6	$N_2H_3 + H \rightarrow 2NH_2$	$k_6 = 2.7 \times 10^{-12}$
R7	$H + H + M \rightarrow H_2 + M$	$k_7 = 8 \times 10^{-33} (300/T)^{0.6}$
R8	$N_2H_3 + N_2H_3 \rightarrow 2NH_3 + N_2$	$k_8 << k_9$
R9	$N_2H_3 + N_2H_3 \rightarrow N_2H_4 + N_2H_2$ $\rightarrow N_2H_4 + N_2 + H_2$	 $k_9 = 6 \times 10^{-11}$

*In the reactions M is the background gas. †The rate constants k are expressed in cubic centimeters per second for two-body reactions and centimeters to the sixth power per second for three-body reactions. The photodissociation rates $J(NH_3)$ and $J(N_2H_4)$ are in reciprocal seconds. References for the rate constants are cited in Atreya *et al.* (*6*).

might not have terminated with the production of N_2H_4 even when the atmospheric temperature was lower than 150°K. In the primitive atmosphere condensation nuclei may not have been present, and the lifetime of N_2H_4 against condensation may have been longer than its lifetime against photolysis or reaction with H. This may even have been the case if some nuclei were present. But in any case, once the atmosphere had accumulated more than 0.45 bar of CH_4 and H_2, the temperature would have become high enough to allow N_2H_4 to remain in the vapor phase and the $NH_3 \rightarrow N_2$ chemistry would have proceeded. Of course, we cannot be sure that there is enough CH_4 in the atmosphere for this to have occurred, but neither can we rule it out and the assumption is at the very least plausible.

For reference we adopt Hunten's temperature profile and altitude scale (*2*). In Hunten's dry adiabatic model the temperature at the cloud top or surface is 125°K. If no other gas is present, the CH_4 abundance in the upper atmosphere is estimated to be about 2 km-atm (*7*), giving a pressure of about 20 mbar at the cloud top. We have solved one-dimensional steady-state coupled continuity and eddy transport equations for the relevant species, using a generalized Newton-Raphson method. The step size was 1 km, convergence criterion 5 percent, and spectral interval 10 Å. The system was treated as a two-point boundary value problem. The resultant globally averaged profiles of NH_3, NH_2, H, and N_2H_4 volume mixing ratios and the saturation vapor mixing ratio profile of N_2H_4 are shown in Fig. 2. At 125°K, the difference between the calculated N_2H_4 partial pressure and its saturation vapor pressure is almost five orders of magnitude. As the NH_3 photochemical cycle proceeds, more and more N_2 is accumulated in the atmosphere. In approximately 2 percent of geologic time (100 million years) nearly 20 km-atm of N_2 would have been accumulated, raising the cloud top pressure to 350 mbar. With increased pressure more NH_3 would be recycled because of the pressure dependence of the rate of R2. Consequently, less N_2H_4 and therefore less N_2 would be produced. We take this aspect of the evolving atmosphere into account when we calculate the total amount of N_2 accumulated over geologic time.

At the beginning of outgassing from the satellite, when its surface temperature was still at its equilibrium value, only a trace amount of NH_3 could be permitted in the vapor phase. Photolysis of NH_3 at that epoch could take place only near the surface, where its volume mixing ratio relative to 2 km-atm of CH_4 was 5×10^{-8}. Because of its short duration and low atmospheric temperatures, this phase contributed little, if any, of the present-day total N_2 on Titan. As CH_4 accumulated in the atmosphere after outgassing, the surface temperature increased to as much as 150°K. Consequently, the NH_3 vapor pressure increased and photolysis began to occur higher in the atmosphere. In less than 2 percent of geologic time 20 km-atm of N_2 would have accumulated and the cloud top pressure would have increased to 350 mbar. We estimate that 98 percent of the N_2 on Titan was accumulated after the cloud top pressure became high; that is, ≥350 mbar. An accumulation of 20 to 30 km-atm of N_2 also implies a CH_4 abundance on the order of only 0.1 km-atm (*8*) or a cloud top CH_4 partial pressure of 1 mbar. Therefore the profiles of NH_2, H, and N_2H_4 shown in Fig. 2 based on the assumption of a 20-mbar cloud top pressure apply to the atmosphere during an early phase of evolution. For NH_3, however, we show profiles for cloud top pressure of 1 mbar (no N_2, only 100 m-atm of CH_4), 20 mbar (no N_2, but 2 km-

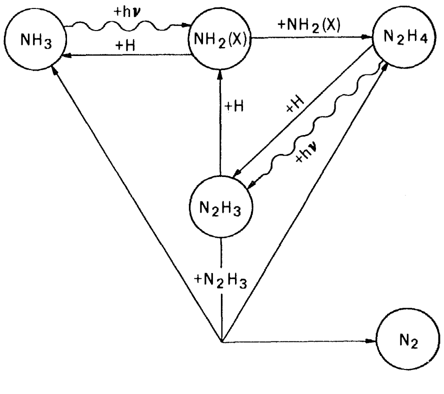

Fig. 1. Schematic of ammonia photochemistry.

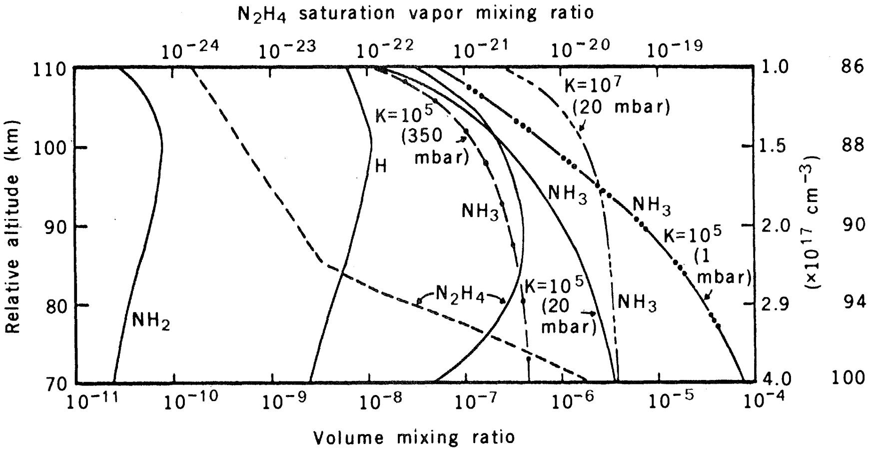

Fig. 2. Volume mixing ratios of NH_3, NH_2, H, and N_2H_4. The solid curves show mixing ratios in an atmosphere with a cloud top pressure of 20 mbar (due to CH_4 alone) and an eddy diffusion coefficient $K = 10^5$ cm^2 sec^{-1}. The height scale is from Hunten (*2*); the corresponding atmospheric densities and temperatures (for a cloud top pressure of 20 mbar) are marked on the right ordinate. The scale for the N_2H_4 saturation mixing ratio is shown on the upper abscissa. Ammonia mixing ratios are also shown for the following cases: (i) $K = 10^5$ cm^2 sec^{-1}, cloud top pressure, 1 mbar (— ··· —) and 350 mbar (—•—); and (ii) $K = 10^7$ cm^2 sec^{-1}, cloud top pressure, 20 mbar (— --- —).

atm of CH_4), and 350 mbar (20 km-atm of N_2). With one exception these results are for an eddy diffusion coefficient $K = 10^5$ cm^2 sec^{-1}. In the high eddy diffusion case ($K = 10^7$ cm^2 sec^{-1}) NH_3 remains mixed to greater altitudes and more photolysis occurs at higher altitudes than in the low case ($K = 10^5$ cm^2 sec^{-1}).

The calculations presented here indicate that a major fraction of the NH_3 outgassed is converted to N_2H_4 or N_2. Both N_2H_4 and N_2 can be recycled to NH_3 only in the presence of an H_2 atmosphere and under conditions of extremely high temperatures and pressures where the activation energies of reactions of NH_2 (produced on thermal decomposition of N_2H_4) or N_2 with H_2 can be overcome. These gas phase reactions occur on Jupiter at H_2 pressures in excess of 3000 bars, a condition that is not likely to occur on Titan. Consequently, once photolyzed, NH_3 is expected to end up in the formation of N_2. The photolysis rate for NH_3 on Titan is 1.2×10^{11} cm^{-2} sec^{-1}. However, NH_2 is reconverted to NH_3 at a rate of 4.4×10^{10} cm^{-2} sec^{-1} if K is 10^7 cm^2 sec^{-1} and 6.4×10^{10} cm^{-2} sec^{-1} if K is 10^5 cm^2 sec^{-1}. Since two NH_2 radicals are required to make each N_2H_4 molecule, this makes the N_2H_4 production rates 3.8×10^{10} and 2.8×10^{10} cm^{-2} sec^{-1}. In reaction R9, two N_2H_3 radicals are needed to produce one molecule of N_2, so the corresponding rates of N_2 production are 1.9×10^{10} and 1.4×10^{10} cm^{-2} sec^{-1}. The total N_2 production over geologic time would be 2.2×10^{27} cm^{-2} for $K = 10^5$ cm^2 sec^{-1} and 2.9×10^{27} cm^{-2} for $K = 10^7$ cm^2 sec^{-1}. This implies a total accumulation of 825 or 1100 km-atm of N_2, corresponding to a pressure of 14 or 19 bars, depending on the two values of K.

In contrast with the mixing ratios of species when the cloud top pressure was only 20 mbar (Fig. 2), the mixing ratios in the present-day atmosphere with a surface N_2 pressure of 14 bars would be 4.5×10^{-7} for NH_3, 3.9×10^{-9} for N_2H_4, 1×10^{-10} for H, and 1×10^{-12} for NH_2 at 70 km, where the temperature is taken to be 100°K. The maximum mixing ratios would be 6.7×10^{-8} for N_2H_4 at 94 km, 1.8×10^{-9} for H at 105 km, and 2×10^{-11} for NH_2 at 103 km. Hunten (*9, 10*) has estimated that a pressure of 21 bars of N_2 would be required to explain the recently measured (*11*) surface temperature of 200°K on Titan. This value of surface pressure is within the range of values we obtain in our models, particularly those with $K = 10^7$ cm^2 sec^{-1}. We are aware of the discrepancy between the "surface" temperatures measured at wavelengths of 3 mm (*11*) and 37 mm (*12*). The latter gives a radio brightness temperature of 115° ± 40°K, much smaller than the recently measured 200°K (*11*). Because of uncertainties in the radius of Titan, it is not apparent whether the lower temperature value applies to the surface or some level high up in the atmosphere. The consequences of possible lower surface temperature on our photochemical model are addressed further in the concluding paragraph.

In reaction R9 one molecule of H_2 is produced for every molecule of N_2. As we have seen, the present rate of N_2 production from NH_3 is 1.4×10^{10} or 1.9×10^{10} cm^{-2} sec^{-1}, depending on the value of K used. Hence, these rates represent lower limits to the rate of escape of H_2 from Titan, assuming limiting flux and no net flux of H_2 into the surface. These are lower limits to the escape flux because additional H_2 can be produced by three-body recombination of H produced in the NH_3 and CH_4 photochemical chain. However, formation of H_2 by reaction R7 in the NH_3 chain is very slow compared to that by R9. In this report we will not discuss CH_4 photochemistry. The H_2 produced in the lower atmosphere will flow upward through the homopause to the base of the exosphere and escape from the atmosphere. Based on the arguments of limiting flux (*1, 13*), we calculate that H_2 produced by NH_3 alone could amount to between 6 and 8 m-atm above the clouds, far less than the 5 km-atm inferred by Trafton (*14*). One should note, however, that Trafton's results represent an upper limit to the H_2 abundance on Titan. On the other hand, recent observations of Münch *et al.* (*15*) place 1 km-atm as an upper limit on the H_2 abundance on Titan. The total amount of H_2 arising from NH_3 in the homosphere is 3 and 5.4 km-atm for the two values of K in our models (*16*). Our calculations also indicate that the density of H_2 at the exobase required to allow H_2 originating from NH_3 to flow away in Jeans escape is 1.4 to 1.9×10^7 cm^{-3}. The exobase density and associated H_2 flux are well within the realm of values required to maintain a Titan torus of approximately 10^3 molecules per cubic centimeter.

The calculations presented here indicate that it is plausible for Titan to have accumulated a thick atmosphere of nitrogen over geologic time, provided the surface temperature during the early phases of evolution was in excess of 150°K. A temperature of 150°K could have been provided by a greenhouse effect, due to either CH_4-H_2 or NH_3. On the other hand, if the surface temperature did not exceed 150°K, the total surface pressure of the resultant N_2 atmosphere would be much smaller than we have calculated, because of inefficient photolysis of N_2H_4. We recognize the possible importance of NH_3 as a contributor to the greenhouse effect (*17*) in addition to CH_4-H_2. Our calculations indicate that for an equilibrium temperature of 86°K the temperature increase due to NH_3 is less than 1°K, but for 120°K it could be about 10°K. Of course this increased surface temperature due to NH_3 would only aid in the production of a nitrogen atmosphere on Titan.

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16. The effusion velocity at the exobase at 120°K is 1×10^3 cm sec^{-1}, while the diffusion velocity at the homopause is only 4×10^{-2} or 4 cm sec^{-1}, depending on whether K is 10^5 or 10^7 cm^2 sec^{-1}. Hence the condition for limiting flux (*1*) is easily met. Therefore, the upward flux of H_2 will be given by bf/H, where the molecular diffusion coefficient of H_2 in N_2 is given by $b/[N_2]$, H is the N_2 scale height at the homopause, and f is the total hydrogen volume mixing ratio attributable to NH_3 in the lower atmosphere. At the homopause temperature of 120°K, b is 1.0×10^{19} cm^{-1} sec^{-1}, H is 26 km, and f is 3.6×10^{-3} or 5×10^{-3} for the two values of K considered. These values of f imply a total H_2 abundance in the homosphere of 3 or 5.4 km-atm. Since the maximum mixing ratio of NH_3 in the photolysis regime is only 4.5×10^{-7} in the presence of 20 km-atm of N_2, the hydrogen must be mainly in the form of H_2. The mixing ratio of CH_4 above the clouds is 5×10^{-3} if there is 20 km-atm of N_2 above the clouds. Hunten (*2*) infers from Strobel's (*4*) treatment of CH_4 photochemistry that there could be an H_2 flux of 9×10^9 cm^{-2} sec^{-1} in addition to the value from NH_3 discussed in the text. This contribution would have to be added to the overall hydrogen budget.
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