

Ammonia Photolysis and the Greenhouse Effect in the Primordial Atmosphere of the Earth

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Photochemical calculations indicate that in the prebiotic atmosphere of the Earth ammonia would have been irreversibly converted to N_2 in less than 40 years if the ammonia surface mixing ratio were $\leq 10^{-4}$. However, if a continuous outgassing of ammonia were maintained, radiative equilibrium calculations indicate that a surface mixing ratio of ammonia of 10^{-5} or greater would provide a sufficient greenhouse effect to keep the surface temperature above freezing. With a 10^{-4} mixing ratio of ammonia, 60 to 70% of the present day solar luminosity would be adequate to maintain surface temperatures above freezing. A lower limit to the time constant for accumulation of an amount of nitrogen equivalent to the present day value is 10 my if the outgassing were such as to provide a continuous surface mixing ratio of ammonia $\geq 10^{-5}$.

INTRODUCTION

The importance of NH_3 to the primitive atmosphere, if indeed it was present, is that its photolysis products could be precursors to prebiotic synthesis (Miller and Urey, 1959) and, in addition, by absorption of longwave radiation NH_3 could produce a substantial "greenhouse effect" and maintain a surface temperature above freezing when the solar output was less than today (Sagan and Mullen, 1972). In this study we have calculated the NH_3 photolysis products produced by solar ultraviolet radiation for several assumed NH_3 atmospheric surface concentrations. We have also made radiation calculations and determined the associated surface temperature increase.

One should note that the primary composition of the prebiotic atmosphere has been a subject of much speculation. Some believe the atmosphere consisted primarily of CO , CO_2 , N_2 , and H_2 (Abelson, 1966)

while others consider NH_3 and CH_4 to be important constituents (Sagan and Mullen, 1972; Lasaga *et al.*, 1971). Sagan (1977) has estimated the equilibrium NH_3 mixing ratio to be 3×10^{-5} in the prebiotic atmosphere; for comparison, the NH_3 saturation vapor pressure is 10 bar at $300^\circ K$. For this study we assumed a range of NH_3 surface mixing ratios from 10^{-4} to 10^{-8} .

The background gas is considered inert, i.e., it does not interact with NH_3 photochemical products and is not radiatively active. As we show later this gas may have been primarily nitrogen. If CH_4 were present its photolysis would have occurred higher in the atmosphere as discussed in the following section. We assume a surface pressure of 780 mbar, that of the present day with O_2 excluded. If N_2 is the primary photodecomposition product of NH_3 then this value is reasonable.

The surface temperature calculations are

based on the assumption that with very little or no water vapor there will be no clouds and thus no latent heat release. One might then expect the tropospheric lapse rate to be nearer its dry adiabatic value which depends on the specific heat capacity. The heat capacity for most gases of planetary interest is about $10^7 \text{ ergs}^{-1} \text{ }^\circ\text{K}^{-1}$ making the adiabatic lapse rate 8 to 10°K km^{-1} (see e.g., Morss and Kuhn 1978). We have used the present day value of $9.8^\circ\text{K km}^{-1}$ for calculations of surface temperature. For comparison we do include a calculation with a lapse rate of $6.5^\circ\text{K km}^{-1}$ such as might exist with cloud formation. The actual lapse rate is not crucial to our conclusions.

Estimates for the increase in solar luminosity over geologic time range from 30 to 60% (Sagan and Mullen, 1972). We have included these variations in our calculations.

PHOTOCHEMISTRY OF AMMONIA

In this study we assume that there is no coupling between the ammonia and methane photochemistry primarily since the region of photoabsorption of ammonia is spectrally isolated from that of methane. In addition, if CH_4 were present its photodissociation would occur higher in the atmosphere than the NH_3 photodissociation (see e.g., Atreya and Donahue, 1978; Atreya, Donahue, and Kuhn, 1978) so that the photolysis products would be spatially separated. Also, although the photodissociation of water vapor would reduce the NH_3 concentrations by the reaction $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$, Walker (1976) has estimated that over the first billion years $[\text{OH}]$ was only about 10^5 cm^{-3} , which is too small to influence our results. We have also not included possible influence of hot hydrogen reactions. It is doubtful that they would have significant effect on our ammonia chemistry since the atmospheric number density in the region of ammonia photolysis exceeds 10^{18} cm^{-3} .

Various aspects of ammonia photochemistry have been discussed by Strobel (1975), Ferris and Nicodem (1972), and Nicodem and Ferris (1973). The chemical scheme and numerical techniques we use for NH_3 photochemistry with transport are similar to those presented for an earlier study for the Jovian atmosphere (Atreya *et al.*, 1977). A brief summary of the parameters as they pertain to the primitive earth atmosphere is given below.

The chemical reactions we assumed are shown in Table I and schematically represented in Fig. 1. Photodissociation of NH_3 takes place between 1600 and 2300 Å. The recycling of NH_3 results largely from the three-body recombination reaction, R2, of H with NH_2 produced in the ground state in reaction R1. Only a small fraction of NH_3 is recycled in this manner, and an even smaller fraction by reaction R8. The net result is the eventual conversion of NH_3 to N_2 after a series of reactions, R3 through R9, involving intermediate products such as N_2H_4 and N_2H_3 . From an earlier study by Morss and Kuhn (1978), temperatures in the relevant altitude range of approximately 40 km above the surface were probably comparable to what we observe today and these temperatures are sufficiently high so as to permit N_2H_4 to remain in the gaseous phase. This then allows a direct photodissociation of N_2H_4 and all subsequent reactions follow. Calculations were carried out assuming NH_3 surface mixing ratios by volume of 10^{-4} , 10^{-5} , 10^{-6} , and 10^{-8} . A mixing ratio of 3×10^{-5} corresponds approximately to an equilibrium abundance (Sagan, 1977).

We have included eddy transport in the model although the eddy diffusion coefficient is uncertain, e.g., the dynamics and latent heat release are unknown. We have somewhat arbitrarily assumed the eddy diffusion coefficient to be a constant $10^5 \text{ cm}^2 \text{ sec}^{-1}$ in agreement with present-day tropospheric models. Calculations were also made with a coefficient one-half this

TABLE I
RELEVANT CHEMICAL REACTIONS AND ASSOCIATED RATE CONSTANTS

Reaction number	Reaction	Rate constant ^a	Reference
R1	$\text{NH}_3 + h\nu \rightarrow \text{NH}_2(\text{X}) + \text{H}$	$J(\text{NH}_3)$	Ackerman (1971), Thompson <i>et al.</i> (1963), Watanabe (1954)
R2	$\text{NH}_2(\text{X}) + \text{H} \xrightarrow{+M} \text{NH}_3$	$k_2 = 6 \times 10^{-30}[\text{M}]/(1 + 3 \times 10^{-20}[\text{M}])$	Gorden <i>et al.</i> (1971)
R3	$\text{NH}_2(\text{X}) + \text{NH}_2(\text{X}) \xrightarrow{+M} \text{N}_2\text{H}_4$	$k_3 = 1 \times 10^{-10}$	Gorden <i>et al.</i> (1971)
R4	$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$	$k_4 = 9.87 \times 10^{-12} \exp(-1198/T)$	Stief and Payne (1976)
R5	$\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H}$	$J(\text{N}_2\text{H}_4)$	Ackerman (1971), Schürgers and Welge (1968), Schurath and Schindler (1970)
R6	$\text{N}_2\text{H}_3 + \text{H} \rightarrow 2\text{NH}_2$	$k_6 = 2.7 \times 10^{-12}$	Gehring <i>et al.</i> (1969)
R7	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$k_7 = 8 \times 10^{-34}(300/T)^{0.6}$	Ham <i>et al.</i> (1970)
R8	$\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3 \rightarrow 2\text{NH}_3 + \text{N}_2$	$k_8 \ll k_9$	Stief (1976, personal communication)
R9	$\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3 \rightarrow \text{N}_2\text{H}_4 + \text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}_4 + \text{N}_2 + \text{H}_2$	$k_9 = 6 \times 10^{-11}$	Stief (1976, personal communication)

^a Rate constants k 's (in $\text{cm}^3 \text{sec}^{-1}$) for two-body reactions and ($\text{cm}^6 \text{sec}^{-1}$) for three body reactions. Photodissociation rates $J(\text{NH}_3)$ and $J(\text{N}_2\text{H}_4)$ (in sec^{-1}).

value to determine the influence of eddy transport on the photochemical constituents.

Since some of the rate constants in Table I are temperature dependent it was necessary to assume an atmospheric temperature profile. We assumed a lapse rate of 6°K km^{-1} from the surface to 27 km and an isothermal atmosphere above. The surface temperature was 292°K . This profile corresponds approximately to the primitive atmosphere temperature profiles of Morss and Kuhn (1978). The calculations were found to be insensitive to the choice of spectral intervals smaller than 10 \AA and altitude intervals less than 1 km. One-dimensional coupled continuity and trans-

port equations were then solved for a steady-state case by the Newton-Raphson finite-difference method.

Photodissociation rates of NH_3 are shown in Fig. 2. One notes a large variation in these rates with different surface mixing ratios of NH_3 . As expected, for large values of NH_3 mixing ratio, most of the photodissociation occurs near the top, i.e., above 30 km. For NH_3 mixing ratios of about 10^{-8} , the atmosphere is essentially transparent to the ultraviolet radiation between 1600 and 2300 \AA .

The distributions of NH_3 and its products H , NH_2 , N_2H_3 , and N_2H_4 are shown in Fig. 3. With the exception of NH_3 , these distributions are all for the case in which $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$ and a surface mixing ratio of NH_3 of 10^{-5} . For NH_3 , however, results of a sensitivity study with NH_3 volume mixing ratios of 10^{-4} , 10^{-6} , and 10^{-8} , and one with 10^{-5} but $K = 5 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$ are also shown. In all these cases photolysis leads to a rapid conversion of NH_3 to N_2 ; the concentration of other nitrogen bearing compounds is small. Practically no ultraviolet radiation in the 1600 to 2300 \AA range penetrates to the surface when the NH_3 surface mixing ratio is greater than 10^{-6} . One also notes in

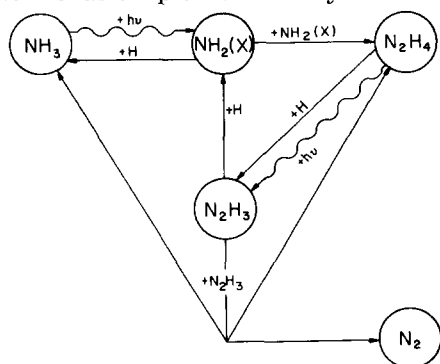


FIG. 1. Schematic representation of the NH_3 photochemistry.

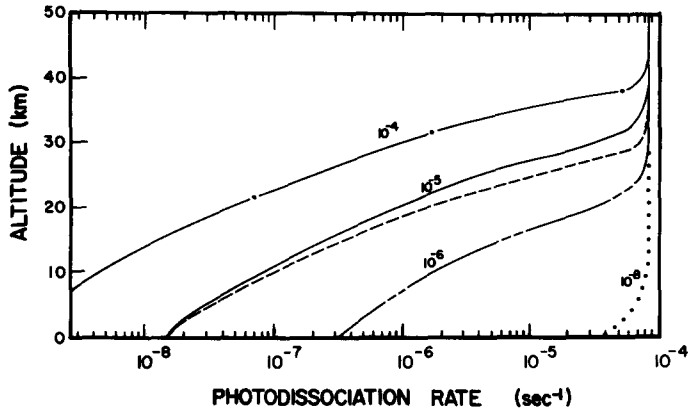


Fig. 2. Photodissociation rates of NH_3 for NH_3 surface mixing ratios of 10^{-4} , 10^{-5} , 10^{-6} , and 10^{-8} with an eddy diffusion coefficient, $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$. The broken line curve is for an NH_3 surface mixing ratio of 10^{-5} but with $K = 5 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$.

Fig. 2 that photolysis to greater depths results when $K = 5 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$ than in the case when $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$. This occurs because in the higher eddy mixing case ammonia remains mixed to greater altitudes thus causing most of the absorption and hence photolysis to take place in the upper altitude range. If the eddy diffusion coefficient were $10^2 \text{ cm}^2 \text{ sec}^{-1}$, then photolysis would occur at the surface and the atmospheric NH_3 concentrations would be much smaller than shown. Furthermore, it should be noted that the

greenhouse effect discussed in the following section is independent of the choice of eddy diffusion coefficient.

AMMONIA GREENHOUSE EFFECT

The possible importance of NH_3 to the greenhouse effect on the primitive Earth has been suggested by Sagan and Mullen (1972) and Sagan (1977). They divided the spectrum into transparent regions corresponding to emission from the Earth's surface and opaque regions corresponding to the absorption bands of the atmospheric

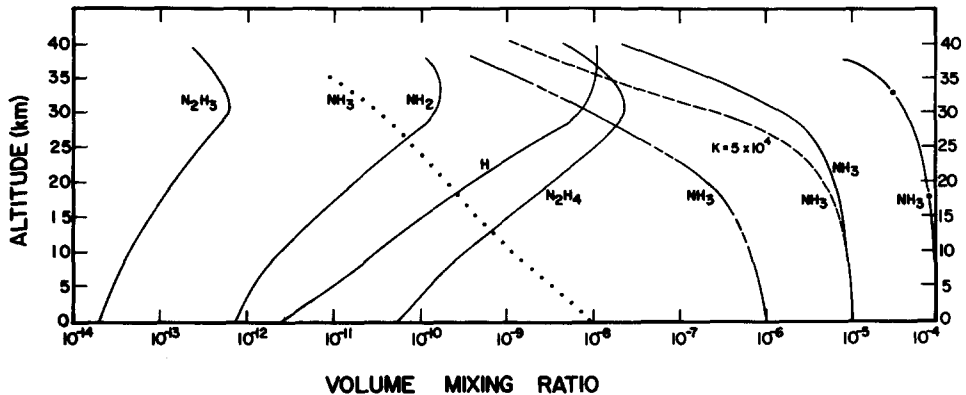


Fig. 3. Volume mixing ratios of NH_3 , H , NH_2 , N_2H_4 , and N_2H_3 with an NH_3 surface mixing ratio of 10^{-5} and an eddy diffusion coefficient $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$ are shown by solid lines. also shown are NH_3 mixing ratio profiles for $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$ and with NH_3 surface ratios of 10^{-4} , 10^{-6} , and 10^{-8} . The broken line curve represents the case for $K = 5 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$ and an NH_3 surface mixing ratio of 10^{-5} .

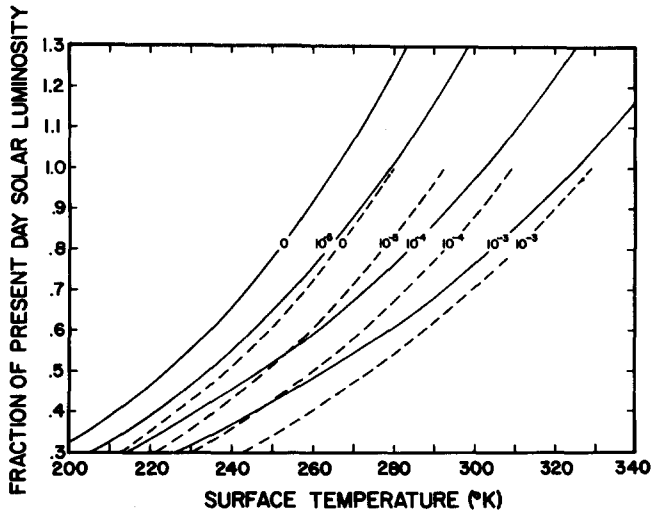


FIG. 4. Mean surface temperatures of the primitive earth for different solar luminosities. Numbers on the curves are the mixing ratios of ammonia. Solid curves are for a lapse rate of $-9.8^{\circ}\text{K}/\text{km}$ with no H_2O present and the dashed curves correspond to a $-6.5^{\circ}\text{K}/\text{km}$ lapse rate and includes the present day H_2O amount.

gases. In the latter case the outward radiation was assumed to originate from the isothermal stratosphere. They then equated the outward thermal radiation to the absorbed solar radiation and determined a mean surface temperature. If the solar luminosity were tens of percent less than today, and the atmospheric composition were the same, then the surface temperature would have been below the freezing point of water, making organic synthesis almost impossible. Sagan (1972) estimated that for an equilibrium abundance of NH_3 with volumetric mixing ratio of 3×10^{-5} , the surface temperature would have been about 320°K for present day solar flux, i.e., a greenhouse effect of about 32°K .

We have calculated from a radiative transfer model (for details see Kuhn *et al.*, 1978) surface temperatures for various NH_3 concentrations and percentages of solar luminosity (Fig. 4). Since the H_2O amount is so uncertain, we have made two separate calculations; one in which the water vapor is absent from the atmosphere and the other utilizing the present day midlatitude water vapor distribution. To allow for a different

albedo than observed today (30%), we have extended the calculations to a solar output of 1.3 times the present value, which corresponds to a 10% albedo for the Earth-atmosphere system. For example, if for the present-day solar flux the albedo were only 20% then the correct value for the ordinate on Fig. 3 would be 1.14. The CO_2 mixing ratio is 4.56×10^{-4} . No ozone was included in the model. The NH_3 mixing ratio varied from 10^{-3} to 10^{-5} . Results indicated the lapse rate was superadiabatic for all NH_3 mixing ratios. Thus a convective adjustment was applied, i.e., the lapse rate was adjusted to be $6.5^{\circ}\text{K km}^{-1}$ for the present day water vapor distribution and equal to the dry adiabatic value of $9.8^{\circ}\text{K km}^{-1}$ when no water vapor was included.

If the atmosphere contained no ammonia then the surface temperature would be between 265 and 280°K depending on the H_2O amount. With the present day H_2O abundance this is still some 8°K below the mean temperature today because the primitive atmosphere we assumed contains no oxygen and thus the total pressure is

only 780 mbar. The thermal radiation to space will therefore be larger, leading to a lowered surface temperature. For an NH_3 mixing ratio of 10^{-5} the greenhouse effect would increase the temperature by some 12 to 15°K. If the lapse rate were adiabatic ($9.8^\circ\text{K km}^{-1}$) and with present day H_2O amounts the surface temperature increase would be close to Sagan's (1977) estimate.

CONCLUSIONS

We have shown that even with significant lowering of the solar luminosity, surface temperatures in the primitive atmosphere could be maintained above freezing if the NH_3 concentration were 10^{-5} or larger; freezing would occur if the luminosity dropped by 10 to 25% depending on the amount of H_2O present. If the concentration were 10^{-4} , then a solar output of only 60 to 70% the present value would be adequate to maintain the temperature above freezing. One must remember, however, that this greenhouse effect could only be maintained so long as there was a continuous source of NH_3 to the atmosphere, presumably by outgassing. Abelson (1966) first suggested that the lifetime of NH_3 would be short because of its photochemical dissociation. We find that if the initial NH_3 mixing ratio was 10^{-4} then in only 40 years the NH_3 would have been destroyed through photolysis. If the mixing ratio were 10^{-5} , then the lifetime was less than 10 years. Thus the NH_3 greenhouse effect would have been restricted to the time over which outgassing occurred.

A significant amount of N_2 could have been produced by NH_3 photolysis. The minimum time for the atmosphere to accumulate an amount of N_2 equal to that of the present day was 10 my if outgassing could have maintained an NH_3 surface mixing ratio of 10^{-5} . The actual time may have been appreciably longer, however, since the photolysis products of NH_3 could also have reacted with other constituents

in the primitive atmosphere such as the hydroxyl radical.

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