

Photochemistry of Nitrogen in the Martian Atmosphere

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Models are developed for the photochemistry of a CO₂-H₂O-N₂ atmosphere on Mars and estimates are given for the concentrations of N, NO, NO₂, NO₃, N₂O₅, HNO₂, HNO₃, and N₂O as a function of altitude. Nitric oxide is the most abundant form of odd nitrogen, present with a mixing ratio relative to CO₂ of order 10⁻⁸. Deposition rates for nitrite and nitrate minerals could be as large as 3 × 10⁶ N equivalent atoms cm⁻² sec⁻¹ under present conditions and may have been higher in the past.

INTRODUCTION

It is now clear that the Martian atmosphere consists mainly of CO₂, with trace quantities of N₂, Ar, H₂O, O₂, CO, and O₃. Carbon dioxide was detected first by Kuiper (1947, 1952), who found unambiguous evidence for the gas in the reflection spectrum of the planet between 1.0 and 2.5 μm. Ground-based spectroscopy also revealed the presence of H₂O (Spinrad *et al.*, 1963; Kaplan *et al.*, 1964; Schorn *et al.*, 1967; Owen and Mason, 1969; Barker *et al.*, 1970; Schorn, 1971), CO (Kaplan *et al.*, 1969; Connes *et al.*, 1969), and O₂ (Carleton and Traub, 1972; Barker, 1972). Ozone was seen first with the ultraviolet spectrometer on Mariner 7 (Barth and Hord, 1971). Nitrogen and argon were observed more recently, with mass spectrometers on Viking 1 (Nier *et al.*, 1976; Owen and Biemann, 1976). Nitrogen is the second-most-abundant constituent, with a mixing ratio of between 2 and 3% relative to CO₂ (Nier *et al.*, 1976; Owen and Biemann, 1976). The mixing ratios for Ar, O₂, and CO are about 1.5% (Nier *et al.*, 1976; Owen and Biemann, 1976), 0.13%

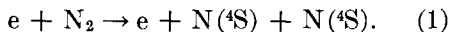
(Carleton and Traub, 1972), and 0.08% (Kaplan *et al.*, 1969), respectively. Water and ozone are variable, with regard to both time and location (Barker, 1976; Barth *et al.*, 1973).

The photochemistry of a CO₂-H₂O system on Mars has been discussed by a number of authors over the past several years (Hunten and McElroy, 1970; Parkinson and Hunten, 1972; McElroy and Donahue, 1972; Liu and Donahue, 1976). Models differ in detail but generally agree that the observed abundances of O₂ and CO are consistent with a photochemical source for these compounds. Models also predict that the Martian atmosphere should contain trace quantities of H, OH, and HO₂, concentrations of order 10⁵ to 10⁸ cm⁻³, with more abundant quantities of H₂O₂ and H₂. The mixing ratio of H₂, a relatively stable constituent of the Martian environment, could be as large as 10⁻⁵, while the mixing ratio of H₂O₂ could approach 10⁻⁸ (Parkinson and Hunten, 1972; Kong and McElroy, 1976). This paper focuses on additional compounds which one might expect to find in the Martian atmosphere

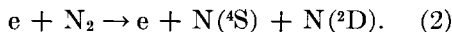
due to the presence of N_2 . A model will be developed to describe the chemistry of a CO_2 - H_2O - N_2 system, and to obtain estimates for the concentrations of N, NO, NO_2 , NO_3 , N_2O_5 , HNO_2 , HNO_3 , and N_2O . The first calculations of nitrogen photochemistry in the Martian atmosphere were performed by Sagan *et al.* (1965), who calculated very low abundances of the oxides of nitrogen. Our model allows for vertical transport of these gases, and explicitly investigates the possible importance of heterogeneous processes at the planetary surface. Several authors (Levine, 1976; Fanale, 1976) have raised the possibility that the bulk of Martian nitrogen may be contained in the regolith, perhaps in the form of nitrate. We shall argue here that atmospheric processes may severely limit the supply of bound nitrogen to the surface, at least under present conditions.

CHEMICAL MODEL

Molecular nitrogen may be dissociated directly by electrons with energies in excess of 9.76 eV,



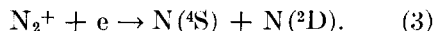
There are indications, however (Oran *et al.*, 1975), that the dominant path for dissociation may involve excitation of valence $b\ ^1\pi_u$ and $b'\ ^1\Sigma_u^+$ states, and Rydberg $c\ ^1\pi_u$ and $c'\ ^1\Sigma_u^+$ states, followed by predissociation through a repulsive $^3\pi_u$ state. Excitation of triplet states by low-energy electrons, followed by a transition to the $^3\pi_u$ state, may also contribute (Oran *et al.*, 1975). In both cases the net reaction may be written in the form



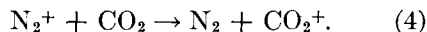
It would appear that (2), rather than (1), should represent the primary path for electron impact dissociation of N_2 .

Dissociative recombination of N_2^+ provides an additional path for dissociation of N_2 in the Martian atmosphere. The most probable path for the reaction, accord-

ing to Michels (1976), involves production of $N(^4S)$ and $N(^2D)$,

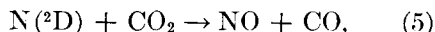


Reaction (3) is less important than (2), however, since N_2^+ in the Martian atmosphere should be removed mainly by



Electrons in (2), and ions in (3), may be formed either by photoionization or by energetic particle bombardment of the Martian atmosphere. Photoionization dominates the net source of fixed nitrogen, although cosmic rays may play a role for the atmosphere below about 30 km (Whitten *et al.*, 1971). A model for the Martian atmosphere, consistent with results from Mariners 6, 7, and 9, is given in Table I (McElroy, 1973). The table includes N_2 and Ar, with mixing ratios for the lower atmosphere set equal to values measured by Viking 1 (Nier *et al.*, 1976; Owen and Biemann, 1976). Concentrations of CO, O, and O_2 were computed using eddy diffusion coefficients tabulated by McElroy and Kong (1976),¹ with a chemical model described by Kong and McElroy (1976). Height profiles for H, OH, HO_2 , O, and O_3 are given in Table II.

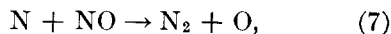
The metastable $N(^2D)$ is quenched efficiently by CO_2 under Martian conditions. It appears (Lin and Kaufman, 1971) that the reaction should proceed through



since the competing reaction



would fail to conserve electron spin. Odd nitrogen would be removed from the Martian atmosphere by



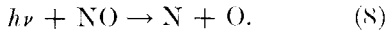
and nitrogen atoms may be formed by (2) and (3), with an important contribution

¹ The eddy diffusion profile has a boundary layer of 100 m, with $K = 10^6 \text{ cm}^2 \text{ sec}^{-1}$.

TABLE I
Model Atmosphere

Z (km)	T ($^{\circ}\text{K}$)	$[\text{CO}_2]$ (cm^{-3})	$[\text{N}_2]$ (cm^{-3})	$[\text{Ar}]$ (cm^{-3})	$[\text{CO}]$ (cm^{-3})	$[\text{O}_2]$ (cm^{-3})
200	364	6.4×10^8	3.5×10^7	1.0×10^7	6.5×10^6	1.5×10^6
190	362	9.8×10^8	4.9×10^7	1.6×10^7	9.2×10^6	2.1×10^6
180	358	1.6×10^9	6.8×10^7	2.5×10^7	1.2×10^7	3.0×10^6
170	354	2.5×10^9	9.5×10^7	4.0×10^7	1.9×10^7	4.4×10^6
160	348	4.3×10^9	1.3×10^8	6.6×10^7	2.7×10^7	6.6×10^6
150	338	7.8×10^9	1.9×10^8	1.1×10^8	4.0×10^7	1.0×10^7
140	325	1.4×10^{10}	3.5×10^8	1.9×10^8	6.5×10^7	1.8×10^7
130	310	2.9×10^{10}	7.3×10^8	4.0×10^8	1.1×10^8	3.8×10^7
120	292	5.8×10^{10}	1.5×10^9	8.0×10^8	2.2×10^8	7.5×10^7
110	265	1.2×10^{11}	3.0×10^9	1.7×10^9	5.5×10^8	1.6×10^8
100	220	2.9×10^{11}	7.3×10^9	4.0×10^9	1.3×10^9	3.8×10^8
90	180	9.0×10^{11}	2.3×10^{10}	1.2×10^{10}	3.0×10^9	1.2×10^9
80	155	4.0×10^{12}	1.0×10^{11}	5.5×10^{10}	8.0×10^9	5.2×10^9
70	138	1.7×10^{13}	4.3×10^{11}	2.4×10^{11}	2.2×10^{10}	2.2×10^{10}
60	125	7.6×10^{13}	1.9×10^{12}	1.1×10^{12}	6.1×10^{10}	9.9×10^{10}
50	122	3.4×10^{14}	8.5×10^{12}	4.7×10^{12}	2.7×10^{11}	4.4×10^{11}
40	126	1.6×10^{15}	4.0×10^{13}	2.2×10^{13}	1.3×10^{12}	2.1×10^{12}
30	133	7.0×10^{15}	1.8×10^{14}	9.7×10^{13}	5.6×10^{12}	9.1×10^{12}
20	143	2.8×10^{16}	7.0×10^{14}	3.9×10^{14}	2.2×10^{13}	3.6×10^{13}
10	174	9.0×10^{16}	2.3×10^{15}	1.2×10^{15}	7.2×10^{13}	1.2×10^{14}
0	220	1.7×10^{17}	4.2×10^{15}	2.3×10^{15}	1.3×10^{14}	2.2×10^{14}

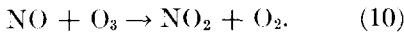
due to predissociation of NO in the δ bands,



A summary of reactions which may be expected to play a role for odd nitrogen in the Martian atmosphere is given in Table III. As we shall see later, NO is the most abundant form of odd nitrogen over a wide range of altitudes. It is removed mainly by



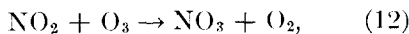
and by



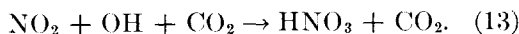
Nitrogen dioxide may be dissociated by sunlight, reforming NO,



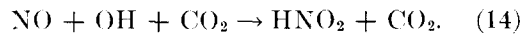
or it may react with O_3 to form NO_3 ,



or with OH to form HNO_3 ,



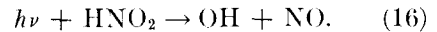
Nitrous acid, HNO_2 , is formed by



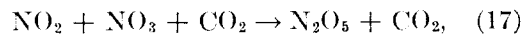
Nitric and nitrous acids are removed by



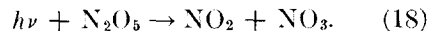
and by



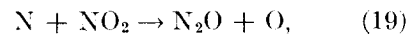
Dinitrogen pentoxide, N_2O_5 , is formed by



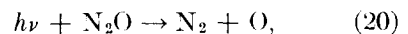
and removed by



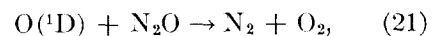
Nitrous oxide may be produced by



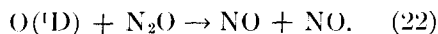
and should be removed by



and by



or by



Rate constants for most of the important reactions in Table III are known with some precision, due largely to extensive efforts over the past several years directed toward the goal of understanding the chemistry of the terrestrial stratosphere [see, for example, the Climatic Impact Assessment Program (1974) or Nicolet (1975)].

RESULTS

We shall explore a number of models, with a variety of assumptions with regard to the possible role of heterogeneous processes at the planetary surface. We focus initially on models in which the surface is taken as passive, i.e., models in which the flux of individual forms of odd nitrogen may be assumed to vanish at height $Z = 0$. We shall refer to passive models by the symbol A. Models B will allow for surface adsorption of HNO_2 and HNO_3 . Adsorption of HNO_2 and HNO_3 may represent a permanent sink for odd nitrogen, which could be incorporated in the regolith in a variety of possible nitrite and nitrate minerals. Models C will investigate the possibility that surface

reactions may represent a sink for all forms of odd nitrogen. Models C could apply, for example, if Mars had an active biosphere.

The concentration, n_i of a gas i is found by solving a set of coupled equations of the form

$$\begin{aligned} \frac{d\phi_i}{dZ} &= P_i - L_i, \\ \phi_i &= -K \left(\frac{dn_i}{dZ} + \frac{n_i}{H_{av}} \right) \\ &\quad - D \left(\frac{dn_i}{dZ} + \frac{n_i}{H_i} \right), \quad (23) \end{aligned}$$

where the various symbols have their customary significance (Colegrove *et al.*, 1966). The production and loss rates P_i and L_i may depend on the concentration of other gases n_j . We shall allow explicitly for transport of N, NO, HNO_2 , HNO_3 , and N_2O . Concentrations of the most reactive species, NO_3 and N_2O_5 , will be obtained by solving the photochemical equilibrium equations

$$P_j = L_j. \quad (24)$$

Concentrations of H, OH, HO_2 , O, and O_3 are taken from Table II.

Equations (23) are solved subject to the following boundary conditions: for models

TABLE II
Height Distribution of Radicals in the Martian Atmosphere

Z (km)	[H] (cm^{-3})	[OH] (cm^{-3})	[HO_2] (cm^{-3})	[O] (cm^{-3})	[O_3] (cm^{-3})
60	4.8×10^5	2.0×10^1	8.0×10^0	1.9×10^9	2.0×10^4
55	5.0×10^5	1.0×10^2	4.0×10^1	2.2×10^9	1.7×10^5
50	6.0×10^5	5.0×10^2	2.0×10^2	2.8×10^9	1.5×10^6
45	7.0×10^5	2.5×10^3	1.0×10^3	3.2×10^9	7.0×10^6
40	9.5×10^5	1.2×10^4	5.3×10^3	3.8×10^9	3.0×10^7
35	1.4×10^6	6.2×10^4	4.0×10^4	4.2×10^9	1.5×10^8
30	1.8×10^6	2.5×10^5	2.1×10^5	4.0×10^9	5.0×10^8
25	1.8×10^6	6.7×10^5	1.0×10^6	2.5×10^9	1.5×10^9
20	1.1×10^6	9.2×10^5	5.0×10^6	1.2×10^9	2.2×10^9
15	3.4×10^5	5.0×10^5	2.0×10^7	4.8×10^8	2.7×10^9
10	3.4×10^5	3.0×10^5	4.5×10^7	1.9×10^8	2.1×10^9
5	3.0×10^5	2.4×10^5	9.3×10^7	1.0×10^8	1.8×10^9
0	3.0×10^5	2.4×10^5	1.5×10^8	7.9×10^7	2.0×10^9

TABLE III

Reactions and Their Rate Constants for the Nitrogen Photochemistry on Mars^a

$\text{NO} + h\nu \rightarrow \text{N}(^4\text{S}) + \text{O}(^3\text{P})$	$J_1 = 1.724 \times 10^{-4}$
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	$J_2 = 1.767 \times 10^{-3}$
$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$	$J_3 = 4.31 \times 10^{-3}$
$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3$	$J_4 = 3.32 \times 10^{-6}$
$\text{HNO}_2 + h\nu \rightarrow \text{OH} + \text{NO}$	$J_5 = 5.6 \times 10^{-4}$
$\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$	$J_6 = 3.71 \times 10^{-5}$
$\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1\text{D})$	$J_7 = 3.19 \times 10^{-7}$
$\text{N}(^4\text{S}) + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$k_0 = 2.2 \times 10^{-11}$
$\text{N}(^4\text{S}) + \text{OH} \rightarrow \text{NO} + \text{H}$	$k_1 = 6.8 \times 10^{-11}$
$\text{N}(^4\text{S}) + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$k_2 = 1.5 \times 10^{-11} \exp(-3580/T)$
$\text{N}(^4\text{S}) + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	$k_3 = 7.9 \times 10^{-12}$
$\text{N}(^4\text{S}) + \text{NO}_2 \rightarrow \text{NO} + \text{NO}$	$k_4 = 6.1 \times 10^{-12}$
$\text{N}(^4\text{S}) + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$k_5 = 2.0 \times 10^{-12} T^{1/2} \exp(-1200/T)$
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$k_6 = 1.5 \times 10^{-12} \exp(-1330/T)$
$\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$	$k_7 = 6.4 \times 10^{-17}$
$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$k_8 = 6.0 \times 10^{-33} \exp(965/T)$
$\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$	$k_9 = \frac{1.8 \times 10^{-11} \exp(806/T)}{2.3 \times 10^{20} + \text{M}}$
$\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$	$k_{10} = 2.0 \times 10^{-11} \exp(-1200/T)$
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$k_{11} = 1.3 \times 10^{-13} \exp(-2475/T)$
$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	$k_{12} = 9.1 \times 10^{-12}$
$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$k_{13} = \frac{3.5 \times 10^{-13} \exp(880/T)}{2.6 \times 10^{18} + \text{M}}$
$\text{NO}_2 + \text{O} + \text{M} \rightarrow \text{NO}_3 + \text{M}$	$k_{14} = 5.0 \times 10^{-31}$
$\text{HNO}_2 + \text{O} \rightarrow \text{OH} + \text{NO}_2$	$k_{15} = 1.6 \times 10^{-11} \exp(-1860/T)$
$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$k_{16} = 5.0 \times 10^{-13}$
$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$k_{17} = 8.9 \times 10^{-14}$
$\text{HNO}_3 + \text{O} \rightarrow \text{OH} + \text{NO}_3$	$k_{18} = 1.0 \times 10^{-11} \exp(-1860/T)$
$\text{HNO}_3 + \text{H} \rightarrow \text{H}_2 + \text{NO}_3$	$k_{19} = 1.0 \times 10^{-12} \exp(-1180/T)$
$\text{HNO}_3 + \text{H} \rightarrow \text{OH} + \text{HNO}_2$	$k_{20} = 1.0 \times 10^{-11} \exp(-1180/T)$
$\text{NO}_2 + \text{NO}_3 \xrightleftharpoons[\tau]{f} \text{N}_2\text{O}_5^*$	$k_{21} \stackrel{f}{=} 1.0 \times 10^{-12}$
	$k_{21} \stackrel{\tau}{=} \frac{1.0 \times 10^3 + \text{M}}{2.6 \times 10^{19} + \text{M}} + 1.0 \times 10^7$
$\text{N}_2\text{O}_5 + \text{M} \xrightleftharpoons[\tau]{f} \text{N}_2\text{O}_5^* + \text{M}$	$k_{22} \stackrel{f}{=} 0.9 \times 10^{-5} \exp(-9700/T)$
$\text{N}(^4\text{S}) + \text{CO}_2 \rightarrow \text{NO} + \text{CO}$	$k_{23} \stackrel{\tau}{=} 3.7 \times 10^{-11}$
$\text{N} + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{O}$	$k_{24} < 1.0 \times 10^{-19}$
$\text{N} + \text{CO}_2^+ \rightarrow \text{NO}^+ + \text{CO}$	$k_{25} = 1.8 \times 10^{-10}$
$\text{NO} + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{O}_2$	$k_{26} = 1.0 \times 10^{-11}$
$\text{NO} + \text{CO}_2^+ \rightarrow \text{NO}^+ + \text{CO}_2$	$k_{27} = 6.3 \times 10^{-10}$
$\text{NO}^+ + \text{e}^- \rightarrow \text{N}(^2\text{D}) + \text{O}$	$k_{28} = 1.2 \times 10^{-10}$
$\text{N}(^2\text{D}) + \text{CO}_2 \rightarrow \text{NO} + \text{CO}$	$k_{29} = 1.0 \times 10^{-7} \exp(T/1000)^{-1.5}$
$\text{N}_2 + \text{e}^-(\text{fast}) \rightarrow 2\text{N}(^2\text{D}) + \text{e}^-$	$k_{30} = 1.8 \times 10^{-13}$
$\rightarrow 2\text{N}(^4\text{S}) + \text{e}^-$	$k_{31} \left. \vphantom{k_{30}} \right\} \text{See text}$

^a The units for mean photolysis rates (J) and two-body and three-body reactions (k) are sec^{-1} , $\text{cm}^3 \text{sec}^{-1}$ and $\text{cm}^6 \text{sec}^{-1}$, respectively. Numerical values for J_1 through J_7 apply under optically thin conditions. This table is taken from McConnell and McElroy (1971), with all three-body reaction rates increased by a factor of 1.5 to account for the third-body effect of CO_2 (DeMore, private communication, 1976).

TABLE III—Continued

$N_2O + O(^1D) \rightarrow 2NO$	$k_{32} = 3.0 \times 10^{-10} \exp(430/T)$
$N_2^+ + e^- \rightarrow N(^2D) + N(^2D)$	k_{33}
$\quad \rightarrow N(^2D) + N(^4S)$	k_{34}
$\quad \rightarrow N(^4S) + N(^4S)$	k_{35}
$N_2^+ + O \rightarrow NO^+ + N(^2D), 90-100\%$	$k_{36} = 1.4 \times 10^{-10} \left[\frac{300}{T_i} \right]^{0.44}$
$\quad \rightarrow NO^+ + N(^4S), 0-10\%$	
$N_2^+ + NO \rightarrow NO^+ + N_2$	$k_{37} = 3.3 \times 10^{-10}$
$N^+ + CO_2 \rightarrow CO_2^+ + N$	$k_{38} = 1.3 \times 10^{-9}$
$N^+ + CO \rightarrow CO^+ + N$	$k_{39} = 5.0 \times 10^{-10}$
$N^+ + O_2 \rightarrow O_2^+ + N$	$k_{40} = 3.0 \times 10^{-10}$
$N^+ + O_2 \rightarrow NO^+ + O$	$k_{41} = 3.0 \times 10^{-10}$
$N^+ + NO \rightarrow NO^+ + N$	$k_{42} = 8.0 \times 10^{-10}$
$O^+ + N_2 \rightarrow NO^+ + N(^4S)$	$k_{43} = 6.0 \times 10^{-13}$
$O^+ + NO \rightarrow NO^+ + O$	$k_{44} = 2.0 \times 10^{-11}$

A, $\phi_i \rightarrow 0$ as $z \rightarrow \infty$, and as $z \rightarrow 0$, for all species i ; for models B, $\phi_i \rightarrow 0$ as $z \rightarrow \infty$ and as $z \rightarrow 0$ except for HNO_2 and HNO_3 , for which $\phi_i = -\gamma_i n_i v_i$ at $z = 0$. The reaction coefficients γ_i are allowed to assume a range of possible values: v_i is the thermal velocity of species i .

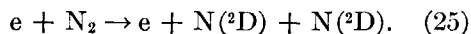
Figures 1 and 2 illustrate results obtained with model A.² Nitric oxide is the most abundant form of odd nitrogen, followed by NO_2 , N_2O , HNO_2 , and HNO_3 , for the atmosphere below 60 km, except for a thin layer near the ground where HNO_3 may be more abundant than HNO_2 . Nitric oxide remains important at higher altitudes. The upper atmosphere includes a significant concentration of N, about 10^6 cm^{-3} near the ionospheric peak at about 130 km. Sources and sinks for odd nitrogen are shown in Fig. 3. Production of odd nitrogen by ionospheric reactions above 100 km is balanced by reaction (7) near 110 and 20 km.

² We do not explicitly include a calculation for the concentration of N_2O_4 , a dimer of NO_2 discussed by Sagan *et al.* (1965). The concentration of N_2O_4 can be estimated to be $\sim 10 \text{ cm}^{-3}$ near the surface using the data by Johnston and Graham (1974) and Hampson and Garvin (1975). It is unlikely, therefore, that the "blue haze" discussed by Sagan *et al.*, (1965) can be attributed to N_2O_4 . A more probable explanation is preferential absorption of sunlight by the pink dust.

The results in Figs. 1 and 2, as indicated by solid lines, assume that approximately 50% of the nitrogen atoms formed by dissociation of N_2 are released in the 2D state. If (1) rather than (2) were to represent the major path for dissociation of N_2 , the concentration of NO would be reduced by about a factor of 4 and the profiles for various species would be modified as shown by the dashed lines in Figs. 1 and 2.

Figure 4a shows a profile for the zenith intensity of Martian dayglow in the 1-0 γ band of NO, as calculated using a scattering factor, g , for sunlight equal to $3.3 \times 10^{-6} \text{ sec}^{-1}$ (Barth, 1966). Figure 4b shows similar results for the limb intensity of the dayglow, with a geometry appropriate for the observations carried out by Mariner 9 (Hord *et al.*, 1970).

It is clear from the Mariner 9 data, and from the earlier measurements by Mariners 6 and 7, (Barth *et al.*, 1971) that the limb intensity, for a tangent height of 135 km, must be less than about 6 kR (Barth, 1976). The present results are consistent with this limit. Figure 4 includes also a model in which the dominant path for electron impact dissociation of N_2 was taken as



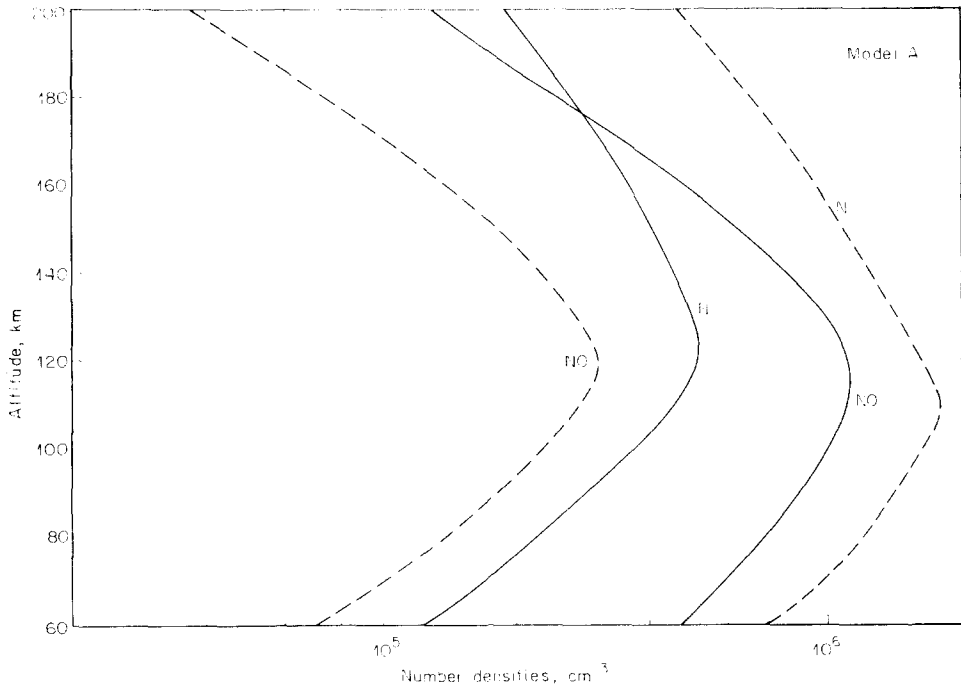


FIG. 1. Number densities of N and NO as computed for the Martian upper atmosphere. The solid lines denote results for the case in which $e + N_2 \rightarrow N(^4S) + N(^4S) + e$ is taken to represent the major path for dissociation of N_2 . Dashed lines denote results for the case in which dissociation is assumed to proceed through $e + N_2 \rightarrow N(^4S) + N(^2D) + e$.

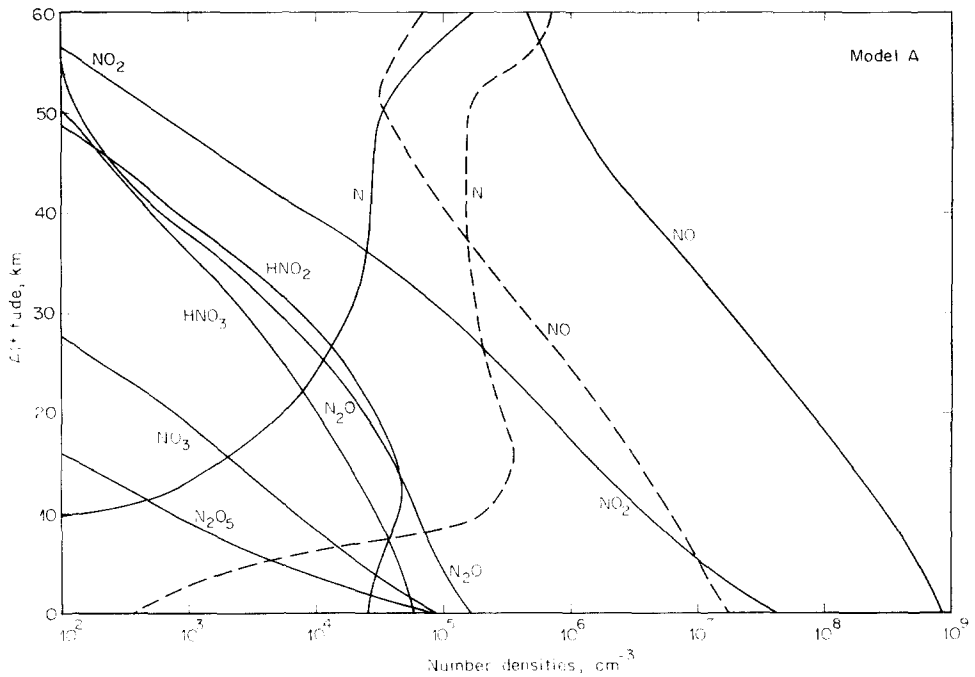


FIG. 2. Number densities of N, NO, NO_2 , NO_3 , N_2O , HNO_2 , HNO_3 , and N_2O_5 in the lower atmosphere. Solid and dashed lines have the same significance as in Fig. 1.

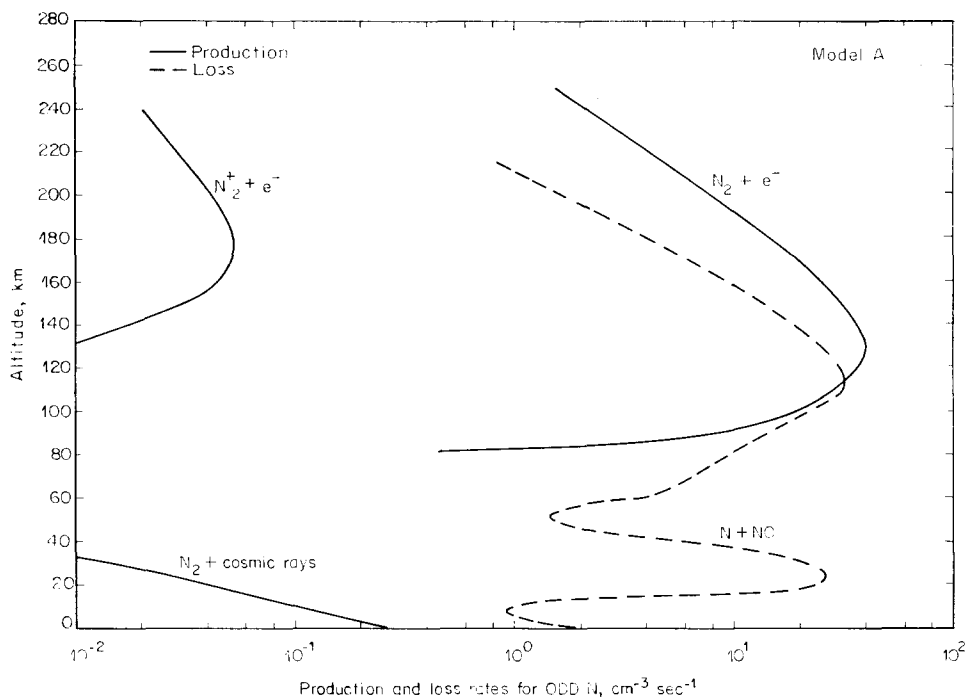


FIG. 3. Production rates for odd N due to electron impact dissociation, dissociative ionization, and cosmic ray bombardment together with loss rates for odd N due to the reaction $N + NO \rightarrow N_2 + O$.

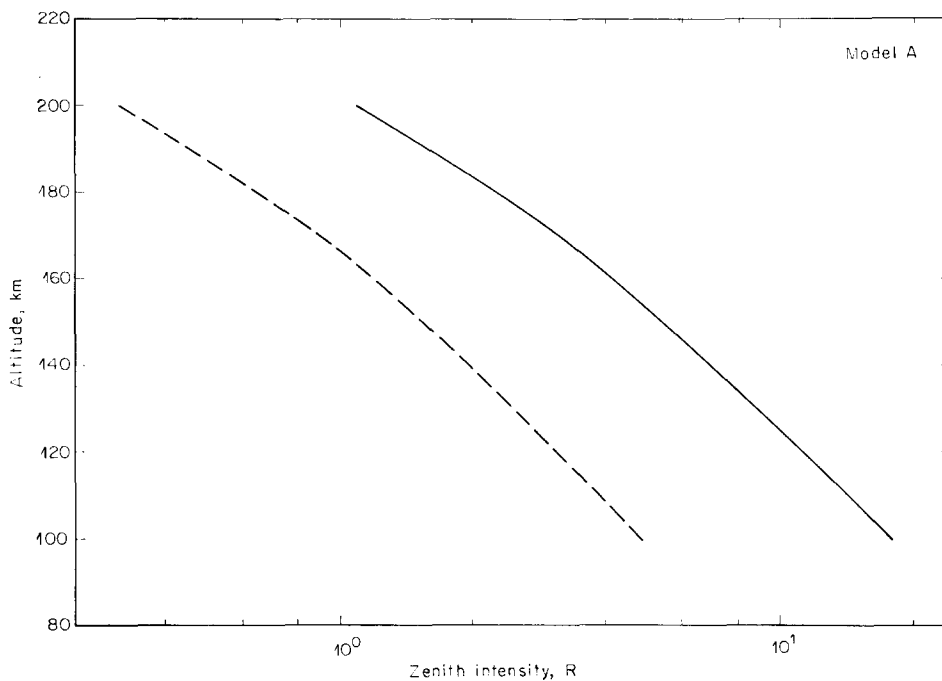


FIG. 4a. Zenith intensities for the 1-0 γ band of NO, in Rayleighs for the NO profiles shown in Fig. 1.

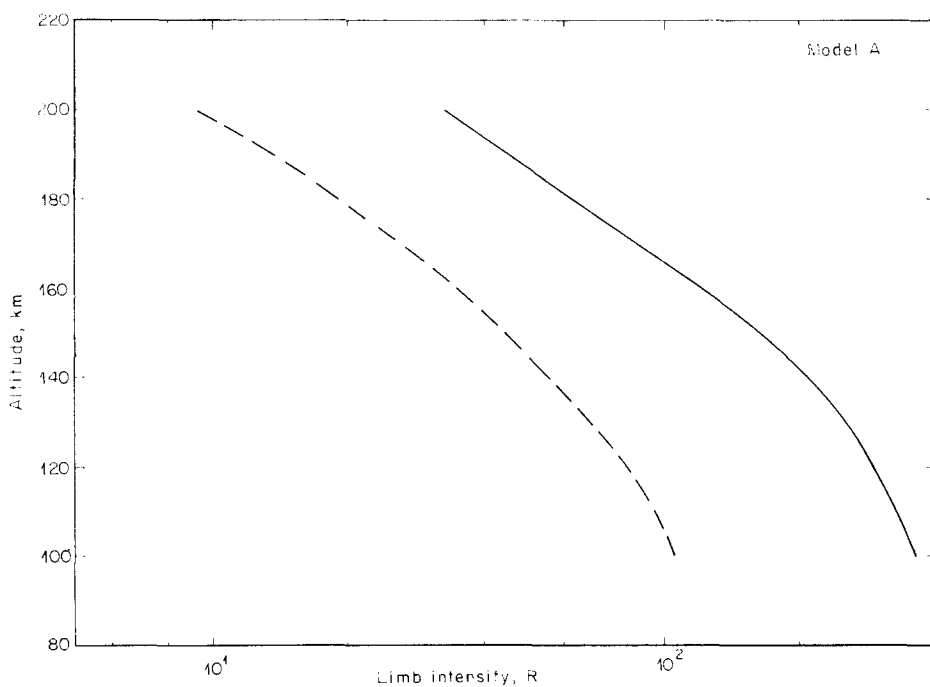


FIG. 4b. Limb intensities for the 1-0 γ band of NO, for the NO profiles shown in Fig. 1.

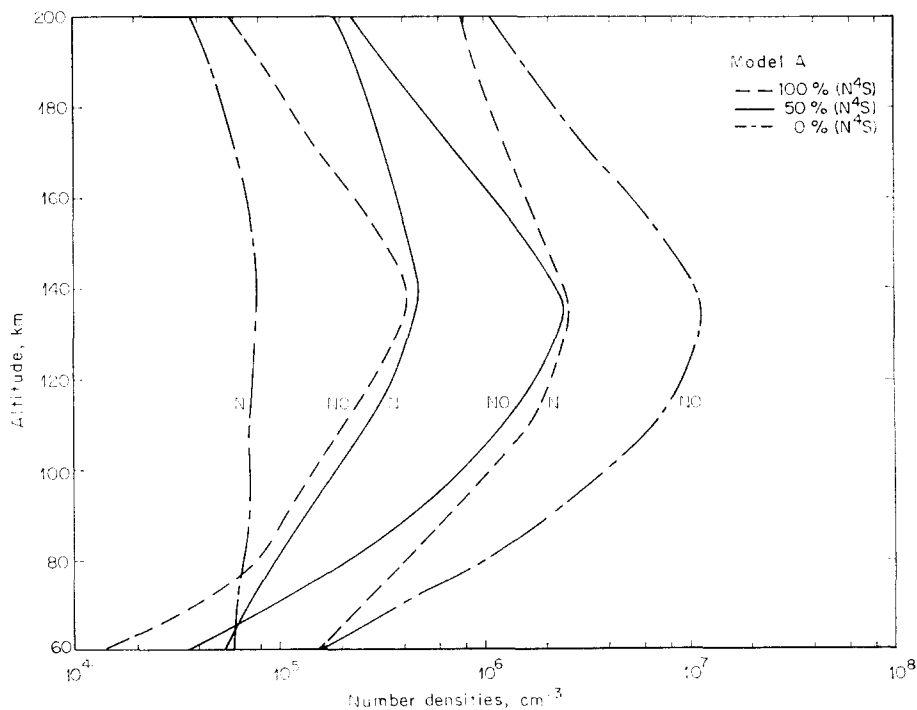


FIG. 5. Number densities of N and NO as obtained with a model in which the eddy diffusion coefficient was reduced by a factor of 30 above 50 km. The three cases correspond to yields of N(S) due to electron impact dissociation of N_2 of 100, 50, and 0%, respectively.

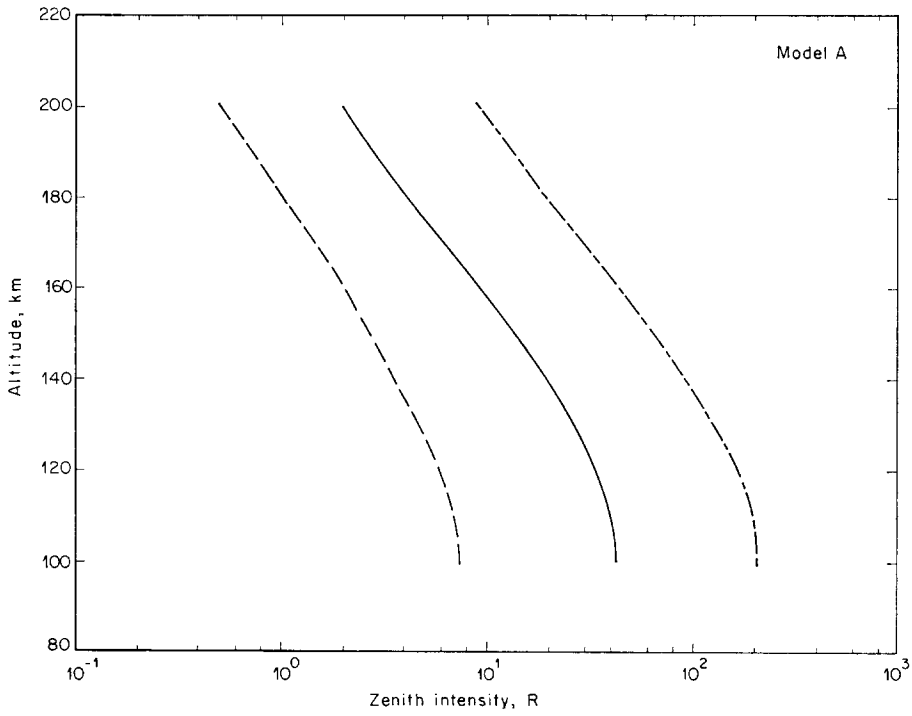


FIG. 6. Zenith intensities for the 1-0 γ band of NO for the NO profiles shown in Fig. 5.

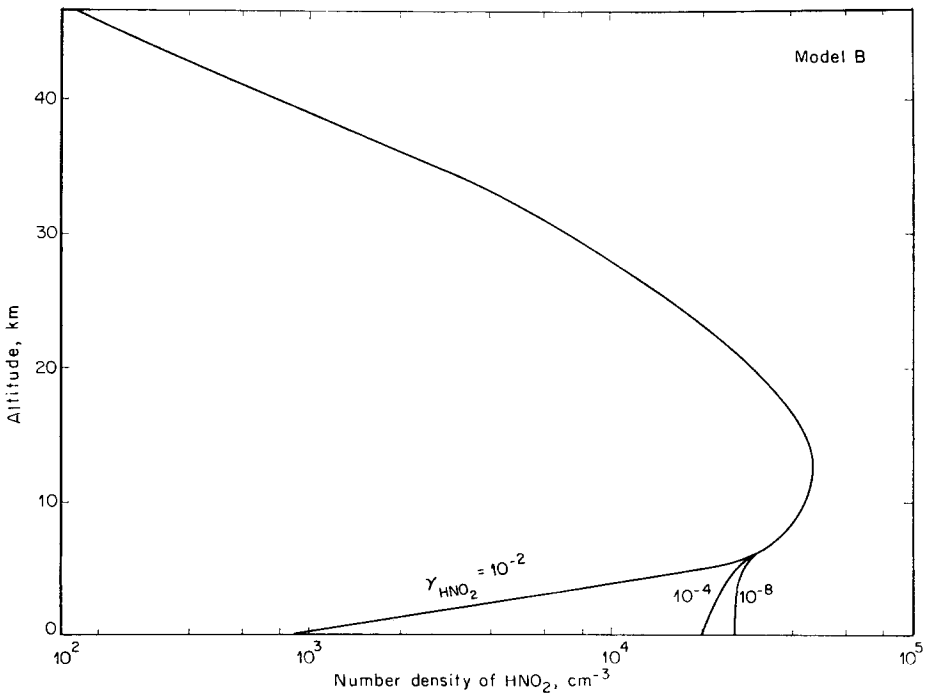


FIG. 7. Number densities for HNO_2 with the yield of $\text{N}(^4\text{S})$ taken equal to 50% with γ_{HNO_2} equal to 10^{-2} , 10^{-4} , and 10^{-8} , with γ_{NO} set equal to 0.

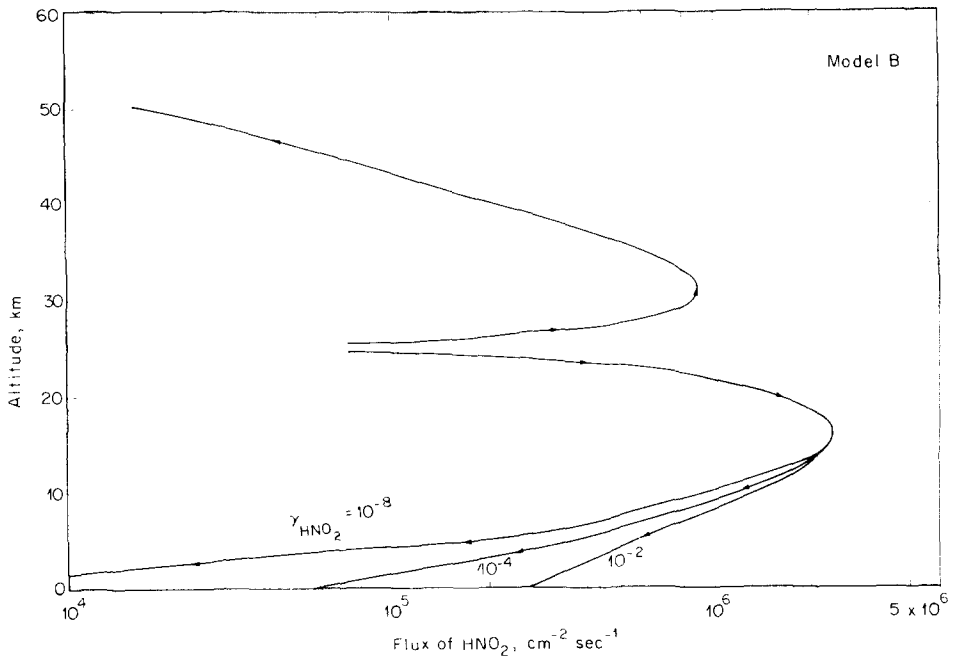


FIG. 8. Fluxes of HNO_2 with the same assumptions as in Fig. 7.

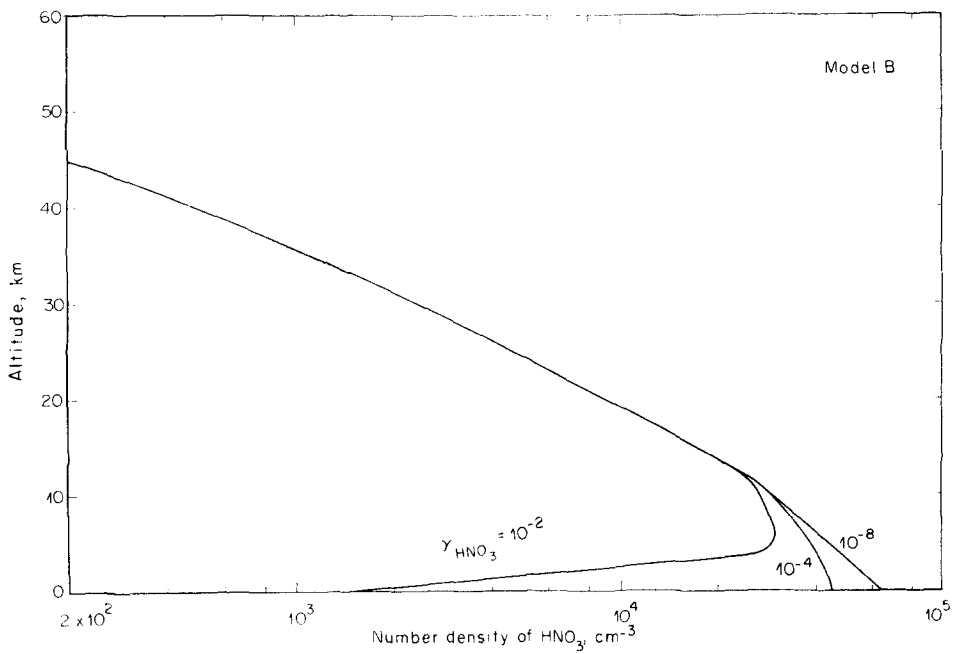


FIG. 9. Number density of HNO_3 with the yield of $\text{N}(^4\text{S})$ equal to 50%, with γ_{HNO_3} equal to 10^{-2} , 10^{-4} , and 10^{-8} , with γ_{NO} equal to 0.

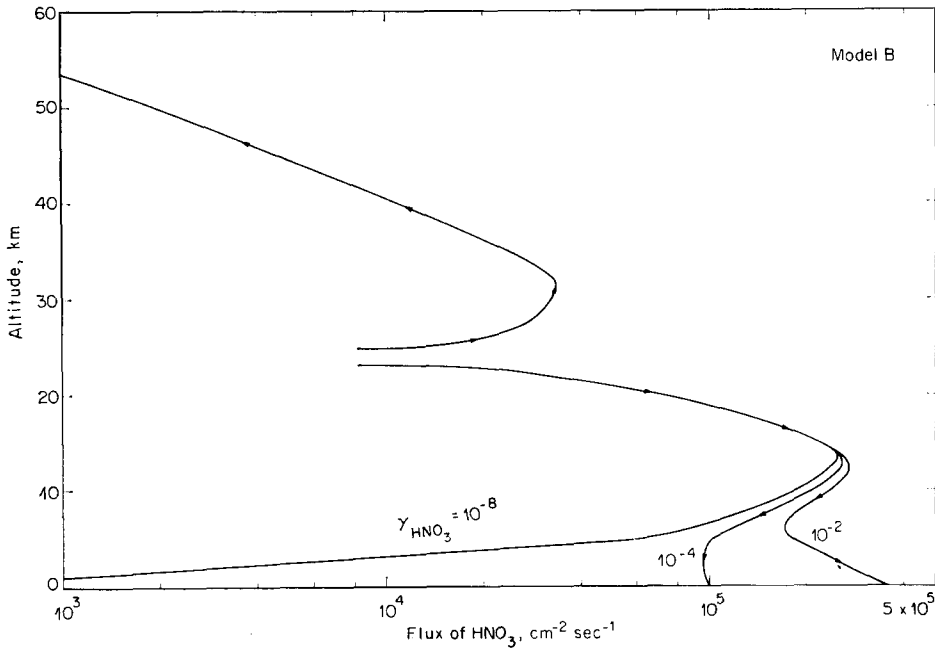


Fig. 10. Fluxes of HNO_3 computed with the same assumptions as in Fig. 8.

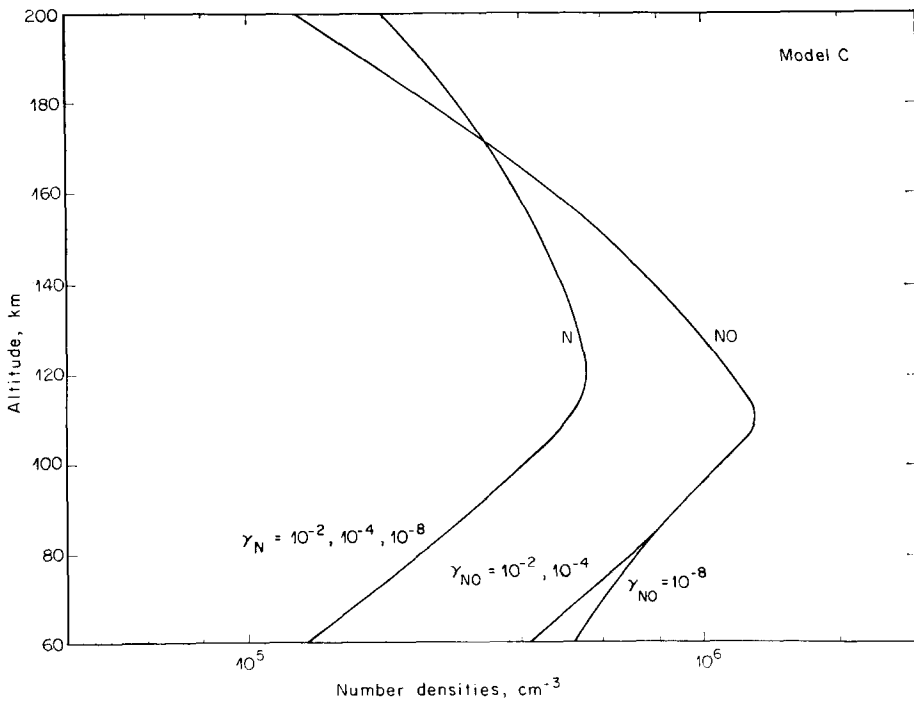


Fig. 11. Number densities of N and NO in the upper atmosphere for various values of γ_N and γ_{NO} . The N(⁴S) yield is taken equal to 50%.

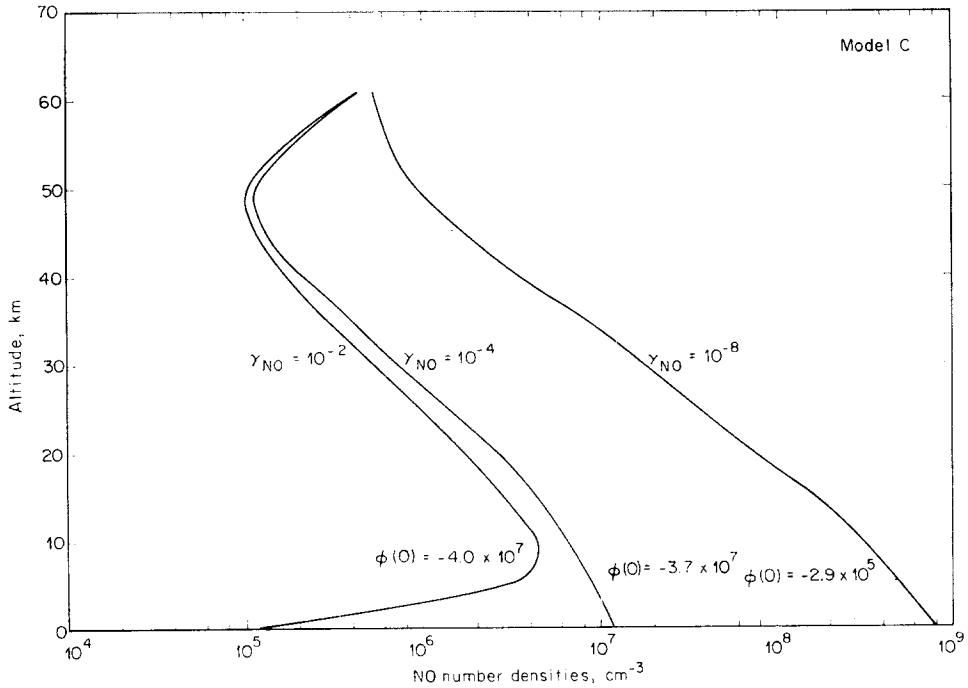


Fig. 12. Number densities of NO in the lower atmosphere with γ_{NO} equal to 10^{-2} , 10^{-4} , and 10^{-8} . Assumptions are the same as in Fig. 11. Fluxes of NO at the surface are given in units of molecules $\text{cm}^{-2} \text{sec}^{-1}$.

Results in this case also agree with the Mariner limit. Mixing ratios calculated for the various forms of odd nitrogen in the lower atmosphere are in accord with upper limits quoted by Owen and Sagan (1972).

Figure 5 shows results obtained using a model in which the eddy coefficient was reduced by about a factor of 30 above 50 km. The resulting intensities for the 1-0 γ band emission from NO are given in Fig. 6.

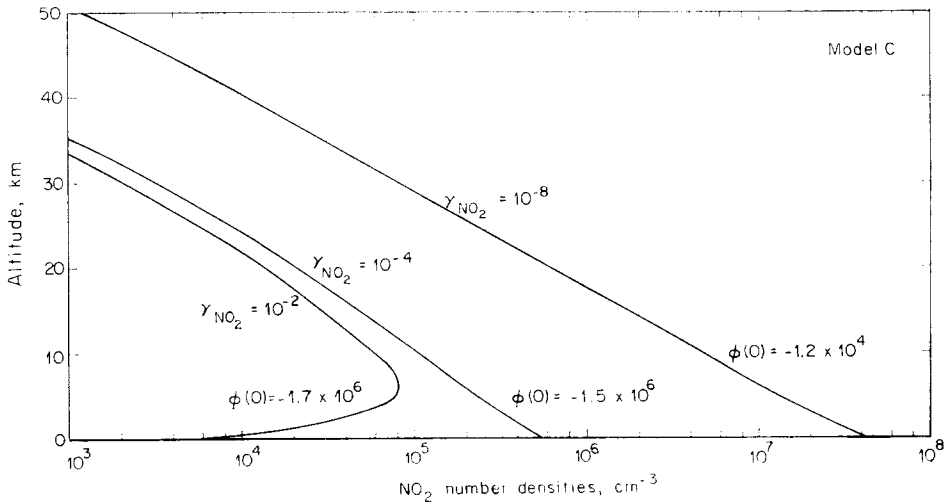


Fig. 13. Number densities of NO_2 : assumptions same as in Fig. 12.

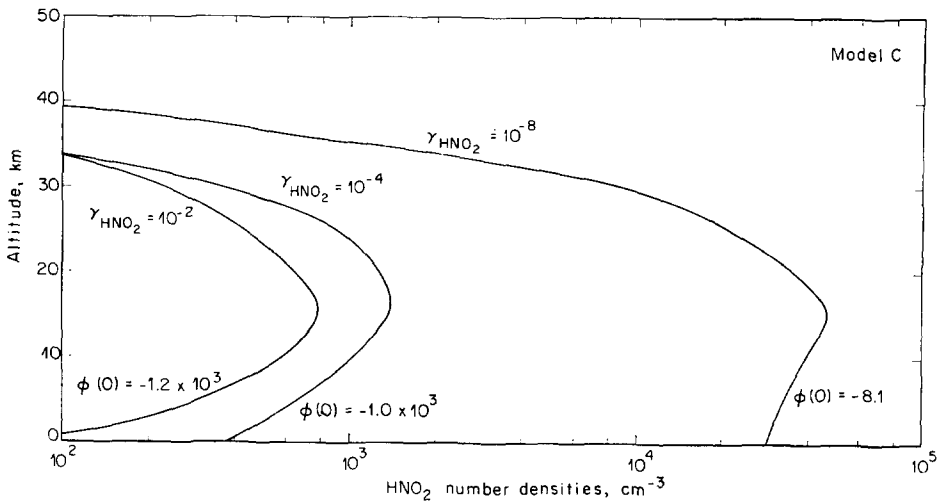


FIG. 14. Number densities of HNO₂: assumptions same as in Fig. 12.

It is clear that upper regions of the Martian atmosphere must be exceedingly well mixed. Results shown in Fig. 6 would approach the limit imposed by Mariner 9. Results obtained with model B are shown in Figs. 7 to 10. Figures 7 and 8 give density profiles and the fluxes of HNO₂ for various values of γ . Corresponding results for HNO₃ are shown in Figs. 9 and 10. The rate for formation of nitrite minerals in Martian soil could be as large as 2.6×10^5 N equivalent atoms $\text{cm}^{-2} \text{sec}^{-1}$

if γ should exceed 10^{-2} . The corresponding rate for deposition of nitrate could be as large as 3.5×10^5 N equivalent atoms $\text{cm}^{-2} \text{sec}^{-1}$.³ Activity coefficients γ may be as high as 10^{-2} for more reactive species on suitable catalytic surfaces.

Results for model C are shown in Figs. 11 to 15. The upper atmospheric profiles

³ We quote these numbers as representative for a reasonably active surface. We shall refine these numbers as we acquire more information about the surface of Mars. The lower limit could be zero if we assume that the surface is not reactive at all.

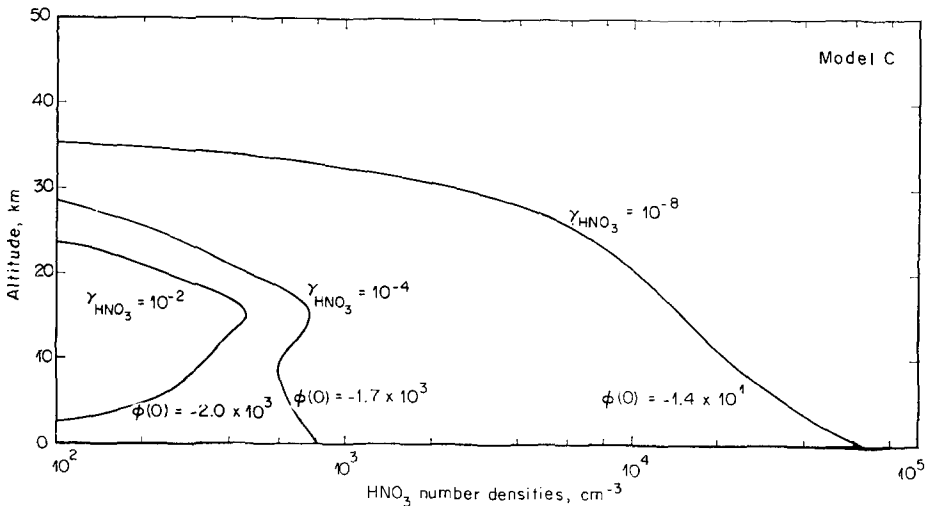


FIG. 15. Number densities of HNO₃: assumptions same as in Fig. 12.

for N and NO are similar to results shown earlier for models A and B. The concentration of NO in the lower atmosphere may be expected to show a direct indication of the possible presence of a heterogeneous sink. The flux of odd nitrogen to the ground could be as large as 4×10^7 N atoms $\text{cm}^{-2} \text{sec}^{-1}$, equivalent to a planetwide source of fixed nitrogen of magnitude 4×10^4 metric tons (N) per year. The source of fixed nitrogen due to lightning in the Earth's atmosphere is believed to be about 2.9×10^9 N atoms $\text{cm}^{-2} \text{sec}^{-1}$ or 1×10^7 metric tons (N) per year (McElroy, 1976). It is clear that the origin and evolution of life on Mars need not be limited by the supply of fixed nitrogen.

CONCLUDING REMARKS

Formation rates for nitrites and nitrates on Mars could be as large as 6×10^5 N equivalent atoms $\text{cm}^{-2} \text{sec}^{-1}$ under present conditions. If we assume that HNO_2 and HNO_3 may be transformed by surface reactions to more stable compounds such as $\text{Ca}[\text{NO}_3]_2$, the atmosphere could supply a surface layer of thickness 0.3 cm in 4.5×10^9 yr. The surface deposit could be much larger if Mars' atmosphere in the past were found to contain more nitrogen than that observed by Viking 1. There are reasons to believe that this should be indeed the case. The escape rate for nitrogen under present conditions could be as large as 1×10^5 atoms $\text{cm}^{-2} \text{sec}^{-1}$ if one were to consider the source of fast exospheric atoms due to (3). Electron impact dissociation of N_2 could provide an escape flux of magnitude comparable to that from (3).

A measurement of NO or NO_2 in the lower atmosphere of Mars would yield valuable information on the role of surface chemistry and could provide a sensitive test for the possible existence of life on the planet.

ACKNOWLEDGMENTS

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