

Wright State University

CORE Scholar

Physics Faculty Publications

Physics

1983

Nitrogen Escape from Mars

Jane L. Fox

Wright State University - Main Campus, jane.fox@wright.edu

Alexander Dalgarno

Follow this and additional works at: <https://corescholar.libraries.wright.edu/physics>



Part of the [Physics Commons](#)

Repository Citation

Fox, J. L., & Dalgarno, A. (1983). Nitrogen Escape from Mars. *Journal of Geophysical Research: Space Physics*, 88 (A11), 9027-9032.

<https://corescholar.libraries.wright.edu/physics/293>

This Article is brought to you for free and open access by the Physics at CORE Scholar. It has been accepted for inclusion in Physics Faculty Publications by an authorized administrator of CORE Scholar. For more information, please contact library-corescholar@wright.edu.

Nitrogen Escape from Mars

J. L. FOX AND A. DALGARNO

Harvard-Smithsonian Center for Astrophysics

The escape rate of nitrogen from Mars is calculated to be $2.3 \times 10^5 \text{ s}^{-1}$ for low solar flux conditions and $8.9 \times 10^5 \text{ s}^{-1}$ for high solar flux conditions. The major source of energetic atoms is dissociative recombination of ground state and vibrationally excited N_2^+ ions. The measured $^{15}\text{N}/^{14}\text{N}$ isotope ratio can be reproduced by postulating an early dense atmosphere during which little differentiation occurred.

1. INTRODUCTION

That substantial quantities of nitrogen have escaped from Mars was suggested by *Brinkmann* [1971], who considered the role of photodissociation in producing nitrogen atoms with energies exceeding the escape energy of about 1.72 eV for the ^{14}N isotope. Support for the escape hypothesis was provided by the Viking mass spectrometer which recorded an anomalous $^{15}\text{N}/^{14}\text{N}$ ratio equal to 1.62 ± 0.16 times the terrestrial value [*Nier and McElroy*, 1977]. Subsequent analyses have investigated other methods for producing energetic nitrogen, including dissociative recombination of N_2^+ [*Yung et al.*, 1977], photoelectron impact dissociation [*Nier et al.*, 1976; *McElroy et al.*, 1977], and chemical reactions [*Fox and Dalgarno*, 1980]. The computed rates for dissociative recombination of N_2^+ ,



and for the reaction



depend on the N_2^+ densities which were not measured by Viking. Only the major ion densities, O_2^+ , CO_2^+ , and O^+ , could be determined by inversion of the RPA measurements from Viking [*Hanson et al.*, 1977]. More detailed data about minor ion densities on Venus have been provided by the mass spectrometers on the Pioneer Venus orbiter [*Taylor et al.*, 1980]. We have refined our calculations to include better estimates of the N_2^+ densities from models which reflect the improved understanding of ion chemistry in CO_2 atmospheres obtained from Pioneer Venus [*Nagy et al.*, 1979, 1980; *Rusch and Cravens*, 1979; *Fox*, 1982]. *Fox* [1982] found that N_2^+ , CO^+ , and N^+ densities on Venus can be reproduced by a model which includes the chemistry of metastable excited states. The reaction



whose rate coefficient has been measured recently [*Rowe et al.*, 1980; *Johnsen and Biondi*, 1980], is a major source of N_2^+ above the exobase on Mars.

The escape rates for ^{15}N and ^{14}N in dissociative recombination of ground state N_2^+ ions differ substantially [*Wallis*, 1978]. The difference is diminished for ions in excited vibrational levels. We have computed the vibrational distribution of N_2^+ at the Martian exobase in order to determine the ^{15}N - ^{14}N fractionation due to dissociative recombination.

Copyright 1983 by the American Geophysical Union.

Paper number 3A1204.
0148-0227/83/003A-1204\$05.00

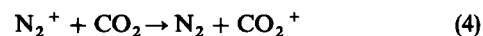
Fanale et al. [1982] have constructed a model of the regolith-atmosphere-polar cap system in which periodic variations occur. We explore their effect on the escape flux of nitrogen.

2. THE MODEL

Our neutral model atmosphere was constructed to reproduce the mass spectrometer measurements from Viking I [*Nier and McElroy*, 1976] except for the O densities, which were derived from the measured $\text{O}_2^+/\text{CO}_2^+$ ratio [*Fox and Dalgarno*, 1979]. Altitude profiles of the neutral densities are presented in Figure 1. The O/ CO_2 ratio is 2% at the ion peak. The neutral, ion, and electron temperatures are those adopted by *Fox and Dalgarno* [1979]. The electron temperatures, which were derived from the measured O_2^+ profile, are lower than the ion temperatures. We will discuss the effect of higher electron temperatures on the escape flux.

Two sets of solar fluxes are considered, the SC 21 reference spectrum, which is appropriate to a period of low solar activity, and the F79050N spectrum, for which $F_{10.7} = 238$ and which is appropriate to a period of high solar activity [*Hinteregger*, 1976; *Torr et al.*, 1979]. We adopted a solar zenith angle of 60° .

The chemical reactions and their rate coefficients are taken from the work of *Fox and Dalgarno* [1979], *Fox and Victor* [1981], and *Fox* [1982]. The coupled continuity and momentum equations were solved for 12 ions and 5 neutral species [*Fox*, 1982]. Altitude profiles of several ions are shown in Figure 2 for low solar activity. The major sources of N_2^+ are photoionization and electron impact ionization below, and the $\text{O}^+(^2D)$ reaction (3) above, 210 km. Reaction (3) produces 35% of the N_2^+ at the exobase near 200 km. Below 215 km, N_2^+ is lost mainly by reaction with CO_2 :

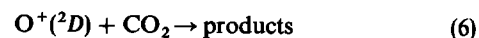


Above 215 km, reactions (R1) and (R2) and the reaction



are more important. The N_2^+ densities shown in Figure 2 are larger than those calculated by *Fox and Dalgarno* [1979] by a factor of 2.5 at 215 km.

The metastable species $\text{O}^+(^2D)$ is relatively more abundant on Mars than on Venus because the densities of electrons and atomic oxygen, which effectively quench the metastable ion, and of CO, which reacts rapidly with it, are lower. The N_2^+ densities on Mars are more sensitive to the rate coefficient for the reaction



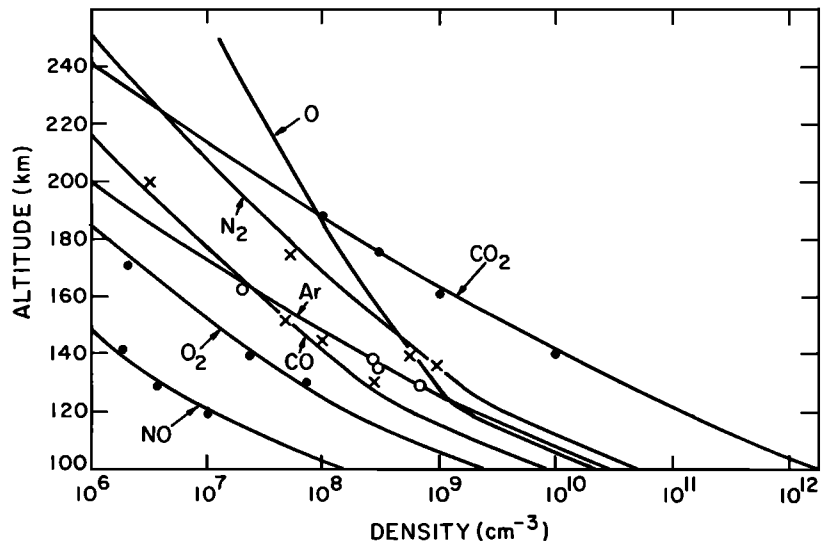
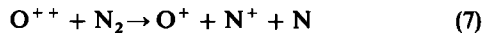


Fig. 1. Altitude profiles of the neutral densities in the model compared to the measured densities of Viking I [Nier and McElroy, 1976]. The CO_2 , O_2 , and NO measurements are represented by circles, the CO and N_2 densities by crosses, and the Ar densities by squares.

a reaction which has not been studied in the laboratory. We assume that $k_6 = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is close to the gas kinetic rate as are the rates for reaction of $\text{O}^+(^2D)$ with N_2 and CO . If $\text{O}^+(^2D)$ does not react with CO_2 then the N_2^+ densities will be enhanced by a factor of 1.3.

The reaction



is a minor source of escaping nitrogen atoms. The sources and sinks of O^{++} have only recently been identified. Victor and Constantinides [1979] found that double photoionization is the major source of O^{++} in the terrestrial ionosphere. They derived cross sections for the process by analogy to those measured for other species and by fitting the threshold behavior to reproduce the O^{++} densities measured on earth. The loss rates for O^{++} by reaction with N_2 , O_2 , Ar , and CO_2 have been measured by Howorka *et al.* [1979] and Johnsen and

Biondi [1978, 1981]. The rate coefficient for the reaction of O^{++} with O was derived by fitting the model O^{++} densities to those measured on Venus [Fox and Victor, 1981].

3. ESCAPE MECHANISMS

Photodissociation occurs by excitation to states in the singlet manifold of N_2 which then decay by predissociation more often than by radiation. The states of the two N atoms which are populated are not the ground states but are some combination of the pairs $^4S + ^2D$, $^4S + ^2P$, and $^2D + ^2D$. We assume that one $\text{N}(^2D)$ is produced in each dissociation, with the remainder of the energy going into kinetic energy of the products.

Prokop and Zipf [1982] have shown that the nitrogen atoms produced in electron impact dissociation of N_2 possess on average only 0.45 eV of kinetic energy so that very few have enough energy to escape from Mars. In contrast, electron

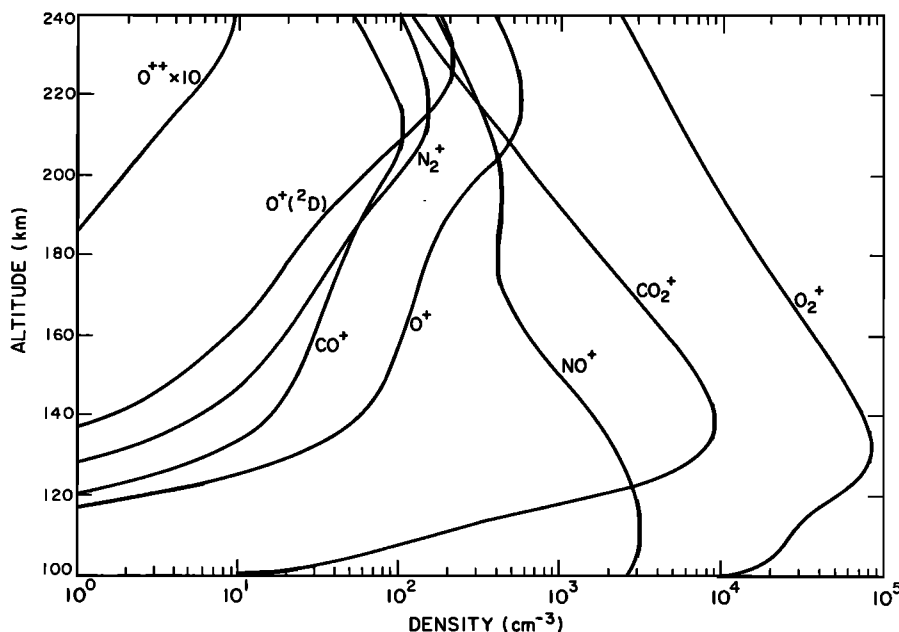


Fig. 2. Altitude profiles of the steady state ion densities in the low solar activity model. The solar zenith angle is 60° .

TABLE 1. Sources and Sinks of Vibrationally Excited N_2^+

Number	Reaction
(R1)	$N_2 + hv \rightarrow N_2^+(X, A, B; v)^* + e$
(R2)	$N_2 + e \rightarrow N_2^+(X, A, B; v) + 2e$
(R3)	$O^+(^2D) + N_2 \rightarrow N_2^+(X, v'' \leq 5; A, v' \leq 1) + O$
(R4)	$O^+(^2P) + N_2 \rightarrow N_2^+(X, v'' \leq 11; A, v' \leq 8) + O$
(R5)	$N_2^+(X, v'') + hv \rightarrow N_2^+(A, v'; B, v')$
(R6)	$N_2^+(X, v'') + e \rightarrow N_2^+(A, v'; B, v') + e$
(R7)	$N_2^+(A, v'; B, v') \rightarrow N_2^+(X, v'') + hv$
(R8)	$N_2^+(X, v'' > 0) + N_2 \rightarrow N_2^+(v < v'') + N_2$
(R9)	$N_2^+(X, v'' > 0) + O \rightarrow N_2^+(v < v'') + O$
(R10)	$N_2^+(X, v'' \geq 5) + O \rightarrow O^+(^2D) + N_2$
(R11)	$N_2^+ + e \rightarrow N + N$
(R12)	$N_2^+ + O \rightarrow NO^+ + N$ $\rightarrow O^+ + N_2$
(R13)	$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$
(R14)	$N_2^+ + CO \rightarrow CO^+ + N_2$

* X is the $X^2\Sigma_g^+$ state, A is the $A^2\Pi_u$ state, and B is the $B^2\Sigma_u^+$ state of N_2^+ .

impact dissociative ionization produces energetic nitrogen atoms and ions [cf. *Morgan and Mentall*, 1983]. We assume that electron impact dissociation is not a source of escaping nitrogen atoms, but that in dissociative ionization, electrons, and photons with energies greater than 28 eV produce N atoms with sufficient energy to escape.

Reaction (2) produces an $N(^2D)$ atom with less than the escape energy at least 90% of the time [*Frederick and Rusch*, 1977]. We assume that 10% of the reactions produce energetic ground state atoms. Although the products in reaction (7) are unknown, we assume that a nitrogen atom is created in every reaction. Then, 10.9 eV are available as kinetic energy of the products, and the nitrogen atoms probably have enough energy to escape.

Dissociative recombination of N_2^+ produces the atom pairs $^4S + ^2D$, $^4S + ^2P$, and $^2D + ^2D$. Consistent with the available data (J. L. Queffelec, personal communication, 1982), we assume the states are populated according to their statistical weights. The atoms have enough energy to escape only when one $N(^4S)$ and one $N(^2D)$ are produced. The energy per atom exceeds the escape energy for ^{14}N but is slightly less than the escape energy for ^{15}N . *Wallis* [1978] argued that a ^{14}N atom produced in dissociative recombination is about twice as likely to escape as a ^{15}N atom. For vibrationally excited N_2^+ , the reaction is more exothermic and the isotope discrimination disappears. Thus for N_2^+ ions in the first excited vibrational state, the reaction is exothermic by 3.71 eV, about twice the escape energy of one ^{15}N .

3.1. The Vibrational Distribution of N_2^+

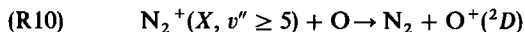
The sources and sinks of vibrationally excited N_2^+ are summarized in Table 1. Photoionization and electron impact ionization ((R1) and (R2)) produce N_2^+ ions in the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states. The branching ratios for photoionization are given by *Samson et al.* [1977] and for electron impact by *Green and Barth* [1965]. The individual vibrational levels are assumed to be populated according to the Franck-Condon factors given by *Nicholls* [1962]. N_2^+ may also be produced in charge transfer reactions of $O^+(^2D)$ and $O^+(^2P)$ with N_2 ((R3) and (R4)). The rate for (R3) has been measured by *Johnsen and Biondi* [1980] and by *Rowe et al.* [1980], who report that $k_3 = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. For reaction (R4) we arbitrarily adopted a rate coefficient of $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

In fluorescent scattering and electron-induced fluorescence,

ground state N_2^+ ions are excited to the $A^2\Pi_u$ or $B^2\Sigma_u^+$ states by the absorption of a photon (reaction (R5)) or by electron impact (reaction (R6)). These states then decay by the emission of a photon (reaction (R7)). The oscillator strengths for excitation of the A and B states are taken from *Cartwright* [1973] and *Degen* [1977]. *Degen* [1977] has computed the solar fluxes averaged over the bands from measurements reported by *Arveson et al.* [1969]. The electron impact cross sections were computed by scaling the cross section for excitation of the $B^2\Sigma_u^+(v' = 0)$ state of *Crandall et al.* [1974] by the factors given by *Degen* [1981]. The transition probabilities for the Meinel ($A-X$) and first negative ($B-X$) bands are given by *Cartwright* [1973] and *Degen* [1977], respectively.

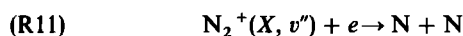
Vibrationally excited $N_2^+(X^2\Sigma_g^+)$ may be lost in chemical reactions. The rate coefficient for collisional relaxation of N_2^+ by N_2 (R8) is about $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [*Smith and Adams*, 1981]. The N_2^+ ions may also be quenched in collisions with atomic oxygen (reaction (R9)). The rate coefficient has not been measured. In order to test the sensitivity of the model to the reaction, we assume that the rate coefficient is either zero or $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

The $N_2^+(X^1\Sigma_g^+)$ ions in vibrational levels $v'' \geq 5$ may undergo charge transfer in collisions with atomic oxygen

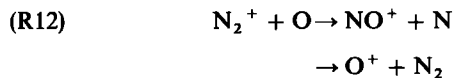


producing $O^+(^2D)$ ions [*Abdou et al.*, 1982]. The reverse reaction, (R3), into levels $v'' \leq 5$ is a major source of N_2^+ at high altitudes on Venus [*Fox*, 1982]. *Abdou et al.* view the reaction as a resonance process and argue that $k_{10} = k_3$. Leaving aside the possibility that (R3) is a source of vibrationally excited $A^2\Pi_u$ ions of N_2^+ [*Omholt*, 1957], only one third of the collisions of N_2^+ and O occur in a doublet spin state so that a probable upper limit to the rate coefficient of (R10) is $\frac{1}{3}k_3$. If resonance considerations are not appropriate the actual value of k_{10} may be much smaller. We assumed that reaction (R3) produces N_2^+ ions in all the vibrational energy levels that are energetically accessible with equal probability.

Zipf [1980] has reported that the rate of coefficient for dissociative recombination of N_2^+ :



depends weakly on the vibrational energy level. We have extrapolated his measurements for $v'' = 0, 1, \text{ and } 2$ to obtain rate coefficients for $v'' = 3-5$. We assume the rates for loss of N_2^+ by reaction with O , CO_2 , and CO ((R10)–(R12)) to be independent of the vibrational energy level. *McFarland et al.* [1974] have studied the reaction



and reported a rate coefficient of $1.4 \times 10^{-10} (T/300)^{-0.44}$ with O^+ produced about 7% of the time. *Smith et al.* [1978] and *Chen et al.* [1978] have measured the rate coefficients for reactions (R13) and (R14) and give $k_{13} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $k_{14} = 7.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

The resulting vibrational distribution of N_2^+ at the Martian exobase is presented in Table 2. At and above 200 km, the major source of $N_2^+(X, v'' = 1)$ is fluorescent scattering, whereas at lower altitudes photoionization is of comparable importance. At the exobase, loss due to absorption of a photon is faster than the main chemical loss process, the reaction with CO_2 (R13). Since 40% of N_2^+ ions are vibrationally

TABLE 2. Vibrational Distribution of N_2^+ at 200 km

v''	Relative Population	
	No O Quenching	With O Quenching
0	57%	60%
1	21%	20%
2	10%	10%
3	5.6%	5.2%
4	3.4%	3.1%
5	2.0%	1.9%

excited and since dissociative recombination is faster for vibrationally excited ions, the isotope effect discussed by Wallis [1978] operates only 55% of the time. Quenching by collisions with atomic oxygen has a negligible effect on the vibrational distribution at the exobase.

3.2. Escape Fluxes

Table 3 summarizes the escape fluxes we obtain for both low and high solar activity and their average. Dissociative recombination of N_2^+ produces the largest escape flux of about $2.9 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. Photodissociation produces an escape flux of about $1 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$, reaction (2) $9 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$ and the other sources less than $4 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$. Reaction (7) gives rise to an escape flux of less than $1 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$. The total average escape flux is $5.6 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. The values depend only weakly on the choice of electron temperatures. For an electron temperature profile which exceeds the ion temperatures and which reaches 2000 K near 250 km, the total average escape flux is enhanced by less than 15%.

4. VARIATION OF THE ESCAPE FLUXES WITH TIME

The escape fluxes varied in different ways as the atmosphere evolved. Leovy [1982] has concluded that the assumption of a constant homopause density level on Mars is probably valid. If so, both the turbopause and exobase were higher at earlier times when the atmosphere contained more nitrogen.

Figure 3 shows the escape fluxes as a function of the total mixing ratio of N_2 relative to CO_2 for an arbitrary escape flux at the current N_2 number density. The escape fluxes due to photodissociation, to dissociative ionization of N_2 , and to dissociative recombination of N_2^+ are proportional to the concentration of N_2 at the exobase and for small mixing ratios of N_2 relative to CO_2 to the total column density of N_2 . In the limiting case when the fraction of nitrogen in the atmosphere approaches unity, the column density of N_2 will determine the altitude of the exobase and the escape flux will become constant. The escape fluxes due to chemical sources are pro-

TABLE 3. ^{14}N Escape Fluxes

Process	Low Solar Flux	High Solar Flux	Average
$N_2 + hv \rightarrow N + N$	5.9×10^4	1.4×10^5	1.0×10^5
$N_2 + hv \rightarrow N^+ + N + e$	1.7×10^4	6.0×10^4	3.0×10^4
$N_2 + e \rightarrow N^+ + N + 2e$	1.4×10^4	4.8×10^4	3.1×10^4
$N_2^+ + e \rightarrow N + N$	8.4×10^4	5.0×10^5	2.9×10^5
$N_2^+ + O \rightarrow NO^+ + N$	4.7×10^4	1.3×10^5	8.9×10^4
$N_2 + O^{++} \rightarrow N^+ + N + O^+$	4.8×10^3	1.4×10^4	9.4×10^3
Total	2.3×10^5	8.9×10^5	5.6×10^5

In $\text{cm}^{-2} \text{ s}^{-1}$.

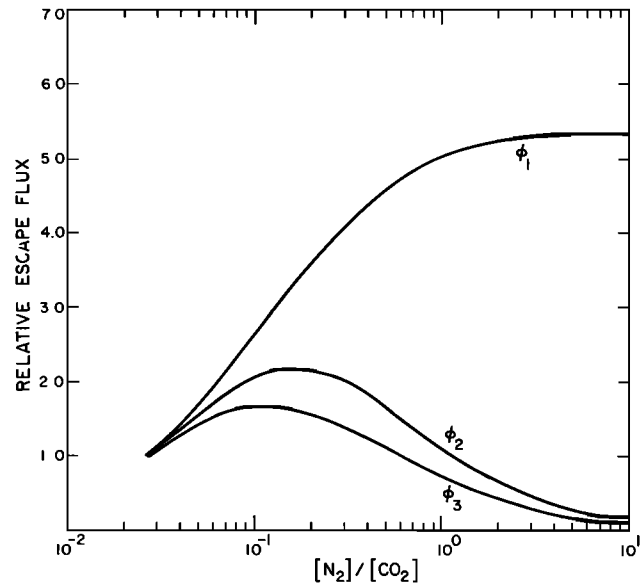


Fig. 3. Relative escape fluxes as a function of the N_2/CO_2 mixing ratio at the turbopause. The flux at the current value of the N_2 mixing ratio, 0.026, is arbitrarily set equal to 1.0; ϕ_1 is the flux proportional to the N_2 density at the exobase, ϕ_2 is the flux due to the reaction $N_2^+ + O \rightarrow NO^+ + N$, and ϕ_3 is the flux due to the reaction $N_2 + O^{++} \rightarrow N^+ + N + O^+$.

portional to O or O^{++} as well as to N_2 . The rate of reaction (2) will achieve a maximum as the concentration of N_2 is increased but then begins to decrease as N_2 becomes the dominant species at the exobase and O decreases. The reaction of O^{++} with N_2 is still more severely damped. As N_2 increases, loss of O^{++} becomes controlled by N_2 . Because the O^{++} density is then inversely proportional to N_2 , the rate of reaction (7) becomes proportional to the atomic oxygen density. Thus the escape fluxes due to chemical reactions are relatively less important at earlier times.

5. INITIAL COLUMN DENSITIES AND ISOTOPE RATIOS

The rate of change of the column abundance, N , of N_2 is

$$dN/dt = -\phi(t)$$

where $\phi(t)$ is the escape flux. The equation for the time evolution of the ratio f of $^{15}N^{14}N$ to $^{14}N^{14}N$ is

$$df/dt = \phi(t)f(1 - R)$$

where R is the net relative escape rate [McElroy et al., 1976; Nier et al., 1976]. R depends on the ratio $^{15}N^{14}N/^{14}N^{14}N$ at the exobase, which is about 0.82 [McElroy et al., 1977], and on the fraction of the escape flux due to dissociative recombination of ground state N_2^+ ions.

By numerical integration over the lifetime of the planet, 4.5×10^9 years, we obtain an initial column density of $1.3 \times 10^{23} \text{ cm}^{-2}$. The calculated isotope enhancement ratio is 2.51, much larger after measured value of 1.62. It appears then that the escape rate was smaller at some time in the past than we predict on the basis of the current value.

Agreement with the measured isotope ratio can be obtained by postulating arbitrarily that the initial outgassing occurred only about $1-2 \times 10^9$ years ago. This late outgassing may not be necessary, however. The isotope enhancement ratio of 2.51 was calculated for an average value of recently measured solar fluxes whereas the intensity may have been different in the

TABLE 4. Isotope Enhancements and Initial Column Densities for Various Regolith Materials

Regolith Material	Isotope Enhancement Ratio	Initial Column Density, molecules cm
None	2.52	1.3×10^{23}
Basalt	2.74	1.5×10^{23}
Nontronite	2.70	1.4×10^{23}

past. Some evidence points to a solar luminosity increasing by a factor of 1.25 to the current value [Newman and Rood, 1977], but arguments based upon models of stellar evolution and observations of young stars suggest that the solar radiation intensity in the ultraviolet was initially about 10^4 times larger than it is today, diminishing to a value perhaps 4 times larger after 1×10^9 years [cf. Zahnle and Walker, 1982; Canuto et al., 1982]. The enhanced solar fluxes would have increased the escape rate but probably reduced the isotopic differentiation [Sekiya et al., 1980].

Isotopic differentiation would be reduced by the alternative hypothesis of an increase in the partial pressure of CO_2 , which would also reduce the escape rate. The CO_2 pressure affects the escape rate of nitrogen because the concentration of N_2 at the exobase is diminished at higher pressures. In the previous calculations we have assumed that the partial pressure of CO_2 on Mars has remained constant throughout the evolution of the planet. Models indicate that Mars has undergone periodic pressure variations [Ward, 1974, 1979] in response to changes in its obliquity and eccentricity. Fanale et al. [1982] have discussed the behavior of the atmosphere, the polar caps, and the regolith resulting from the changes in insolation. We have incorporated these effects into our model by representing the obliquity variations as the product of two sine waves and using the model of Fanale et al. to derive the pressure from the obliquity.

The initial column densities and predicted isotope enhancement ratios for no regolith, basalt regolith, and nontronite regolith models are shown in Table 4. The differences among the models are small because N_2 was a major constituent of the atmosphere throughout most of the lifetime of the planet, when its escape rate was insensitive to the CO_2 pressure. The net escape rate and the isotope ratio in these models are increased. To diminish the isotope ratio, it appears necessary to invoke an early dense atmosphere surviving over a period exceeding 2×10^9 years. If we assume arbitrarily an initial CO_2 pressure of 1 atmosphere diminishing exponentially with a time constant in the range between 7×10^8 and 1×10^9 years to the value today, our calculations do reproduce the measured isotope ratio.

Acknowledgments. This work was supported in part by the National Aeronautics and Space Administration under contract NAS-5-11437 and the National Science Foundation under grant ATM 80-07024.

The Editor thanks Y. L. Yung and another referee for their assistance in evaluating this paper.

REFERENCES

- Abdou, W. A., D. G. Torr, P. G. Richards, and M. R. Torr, The effect on thermospheric chemistry of a resonant charge exchange reaction involving vibrationally excited N_2^+ ions with atomic oxygen, *J. Geophys. Res.*, **87**, 6324, 1982.
- Arveson, J. C., R. N. Griffin, and B. D. Pearson, Determination of extraterrestrial solar spectral irradiance from a research aircraft, *Appl. Opt.*, **8**, 2215, 1969.
- Brinkmann, R. T., Mars: Has nitrogen escaped?, *Science*, **179**, 944, 1971.
- Canuto, V. M., J. S. Levine, T. R. Augustson, and C. L. Imhoff, UV radiation from the young sun and oxygen and ozone levels in the prebiological palaeoatmosphere, *Nature*, **296**, 816, 1982.
- Cartwright, D. C., Transition probabilities for the Meinel band system of N_2^+ , *J. Chem. Phys.*, **38**, 1978, 1973.
- Chen, A., R. Johnsen, and M. A. Biondi, Measurements of the $\text{O}^+ + \text{N}_2$ and $\text{O}^+ + \text{O}_2$ reaction rates from 300 to 900 K, *J. Chem. Phys.*, **69**, 2688, 1978.
- Crandall, D. H., W. E. Kauppila, R. A. Phaneuf, P. O. Taylor, and G. H. Dunn, Absolute cross sections for electron-impact excitation of N_2^+ , *Phys. Rev.*, **A9**, 2545, 1974.
- Degen, V., Modeling of N_2^+ first negative spectra excited by electron impact on N_2 , *J. Quant. Spectrosc. Radiat. Transf.*, **18**, 113, 1977.
- Degen, V., Vibrational enhancement and the excitation of N_2^+ and the first negative system in the high altitude red aurora and the dayside cusp, *J. Geophys. Res.*, **86**, 11,372, 1981.
- Fanale, F. P., J. R. Salvail, W. B. Banerdt, and R. S. Saunders, Mars: The regolith-atmosphere-cap system and climate change, *Icarus*, **50**, 381, 1982.
- Fox, J. L., The chemistry of metastable species in the Venusian ionosphere, *Icarus*, **51**, 248, 1982.
- Fox, J. L., and A. Dalgarno, Ionization, luminosity, and heating of the upper atmosphere of Mars, *J. Geophys. Res.*, **84**, 7315, 1979.
- Fox, J. L., and A. Dalgarno, The production of nitrogen atoms on Mars and their escape, *Planet. Space Sci.*, **28**, 41, 1980.
- Fox, J. L., and G. A. Victor, O^{++} in the Venusian ionosphere, *J. Geophys. Res.*, **86**, 2438, 1981.
- Frederick, J. E., and D. W. Rusch, On the chemistry of metastable atomic nitrogen in the F region deduced from simultaneous satellite measurements of the 5200-Å airglow and atmospheric composition, *J. Geophys. Res.*, **82**, 3509, 1977.
- Green, A. E. S., and C. A. Barth, Calculations of ultraviolet molecular nitrogen emissions from the aurora, *J. Geophys. Res.*, **70**, 1083, 1965.
- Hanson, W. B., S. Sanatani, and D. R. Zuccaro, The Martian ionosphere as observed by the Viking retarding potential analyzers, *J. Geophys. Res.*, **82**, 4351, 1977.
- Hinteregger, H. E., EUV fluxes in the solar spectrum below 2000 Å, *J. Atmos. Terr. Phys.*, **38**, 791, 1976.
- Howorka, F., A. V. Viggiano, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Laboratory studies of O^{++} reactions of ionospheric importance, *J. Geophys. Res.*, **84**, 5941, 1979.
- Johnsen, R., and M. A. Biondi, Measurements of the reaction rates of O^{++} ions with N_2 and O_2 at thermal energies and their ionospheric implications, *Geophys. Res. Lett.*, **5**, 847, 1978.
- Johnsen, R., and M. A. Biondi, Laboratory measurements of the $\text{O}^+(^2D) + \text{N}_2$ and $\text{O}^+(^2D) + \text{O}_2$ reaction rate coefficients and their ionospheric implications, *Geophys. Res. Lett.*, **7**, 401, 1980.
- Johnsen, R., and M. A. Biondi, Reactions of ground-state and metastable O^{2+} ions with He, O_2 , N_2 and CO_2 at thermal energies, *J. Chem. Phys.*, **74**, 305, 1981.
- Leovy, C. B., Control of the homopause level, *Icarus*, **50**, 311, 1982.
- McElroy, M. B., S. L. Yung, and A. O. Nier, Isotopic composition of nitrogen: Implications for the past history of Mars atmosphere, *Science*, **194**, 70, 1976.
- McElroy, M. B., T. Y. Kong, and Y. L. Yung, Photochemistry and evolution of Mars atmosphere: A Viking perspective, *J. Geophys. Res.*, **82**, 4379, 1977.
- McFarland, M., D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, Energy dependence and branching ratio of the $\text{N}_2^+ + \text{O}$ reaction, *J. Geophys. Res.*, **79**, 2925, 1974.
- Morgan, H. D., and J. E. Mentall, EUV studies of N_2 and O_2 produced by low energy electron impact, *J. Chem. Phys.*, **78**, 1747, 1983.
- Nagy, A. F., T. E. Cravens, R. A. Chen, H. A. Taylor, L. H. Brace, and H. C. Brinton, Comparison of calculated and measured ion densities on the dayside of Venus, *Science*, **205**, 107, 1979.
- Nagy, A. F., T. E. Cravens, S. G. Smith, H. A. Taylor, and H. C. Brinton, Model calculations of the dayside ionosphere of Venus: Ionic composition, *J. Geophys. Res.*, **85**, 7795, 1980.
- Newman, M. J., and R. T. Rood, Implications of solar evolution for the Earth's early atmosphere, *Science*, **198**, 1035, 1977.

- Nicholls, R. W., Laboratory astrophysics, *J. Quant. Spectrosc. Radiat. Transf.*, **2**, 433, 1962.
- Nier, A. D., and M. B. McElroy, Structure of the neutral upper atmosphere of Mars: Results from Viking 1 and Viking 2, *Science*, **194**, 1298, 1976.
- Nier, A. O., and M. B. McElroy, Composition and structure of Mars' upper atmosphere: Results from the neutral mass spectrometers on Viking 1 and 2, *J. Geophys. Res.*, **82**, 4341, 1977.
- Nier, A. O., M. B. McElroy, and Y. L. Yung, Isotopic composition of the Martian atmosphere, *Science*, **194**, 68, 1976.
- Omholt, A., The red and near infrared auroral spectrum, *J. Atmos. Terr. Phys.*, **10**, 320, 1957.
- Prokop, T. M., and E. C. Zipf, On the production of kinetically energetic NI atoms by electron impact dissociation of N₂, *Eos Trans. AGU*, **63**, 393, 1982.
- Rowe, B. R., D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton, Rate constants for the reactions of metastable O⁺ ions with N₂ and O₂ at collision energies 0.04 to 0.2 eV and the mobilities of these ions at 300 K, *J. Chem. Phys.*, **73**, 194, 1980.
- Rusch, D. W., and T. E. Cravens, A model of the neutral and ion nitrogen chemistry in the daytime thermosphere of Venus, *Geophys. Res. Lett.*, **6**, 791, 1979.
- Samson, J. A. R., G. N. Haddad, and J. L. Gardner, Total and partial photo-ionization cross sections of N₂ from threshold to 100 Å, *J. Phys. B*, **10**, 1749, 1977.
- Sekiya, M., K. Nakazawa, and C. Hayashi, Dissipation of the primordial terrestrial atmosphere due to irradiation of the solar EUV, *Prog. Theor. Phys.*, **64**, 1968, 1980.
- Smith, D., and N. G. Adams, Charge transfer reaction Ar⁺ + N₂ ⇌ N₂⁺ + Ar at thermal energies, *Phys. Rev. A*, **23**, 2327, 1981.
- Smith, D., N. G. Adams, and T. M. Miller, A laboratory study of the reactions of N⁺, N₂⁺, N₃⁺, N₄⁺, O⁺, O₂⁺, and NO⁺ ions with several molecules at 300 K, *J. Chem. Phys.*, **69**, 308, 1978.
- Taylor, H. A., H. C. Brinton, S. J. Bauer, R. E. Hartle, P. A. Cloutier, and R. E. Daniell, Global observations of the composition and dynamics of the ionosphere of Venus: Implications for the solar wind interaction, *J. Geophys. Res.*, **85**, 7765, 1980.
- Torr, M. R., D. G. Torr, R. A. Ong, and H. E. Hinteregger, Ionization frequencies for major thermospheric constituents as a function of solar cycle 21, *Geophys. Res. Lett.*, **6**, 771, 1979.
- Victor, G. A., and E. R. Constantinides, Double photoionization and doubly charged ions in the thermosphere, *Geophys. Res. Lett.*, **6**, 519, 1979.
- Wallis, M. K., Exospheric density and escape fluxes of atomic isotopes on Venus and Mars, *Planet. Space Sci.* **26**, 949, 1978.
- Ward, W. R., Climatic variations on Mars, 1, Astronomical theory of insolation, *J. Geophys. Res.*, **79**, 3375, 1974.
- Ward, W. R., J. A. Burns, and O. B. Toon, Past obliquity oscillations of Mars: Role of the Tharsis uplift, *J. Geophys. Res.*, **84**, 243, 1979.
- Yung, Y. L., D. F. Strobel, T. Y. Kong, and M. B. McElroy, Photochemistry of nitrogen in the Martian atmosphere, *Icarus*, **30**, 26, 1977.
- Zahnle, K. J., and J. C. G. Walker, The evolution of solar ultraviolet luminosity, *Rev. Geophys. Space Phys.*, **20**, 280, 1982.
- Zipf, E. C., The dissociative recombination of vibrationally excited N₂⁺ ions, *Geophys. Res. Lett.*, **7**, 645, 1980.

A. Dalgarno and J. L. Fox, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138.

(Received March 11, 1983;
revised July 21, 1983;
accepted July 22, 1983.)