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The Production and Escape of Nitrogen Atoms on Mars

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We have computed the production rates and densities of odd nitrogen species in the Martian atmosphere using updated rate coefficients and a revised ionosphere-thermosphere model. We find that the computed densities of NO are somewhat smaller than those measured by Viking 1, but reasonable agreement can be obtained by assuming that the rate coefficient for loss of odd nitrogen in the reaction of N with NO is smaller at temperatures that prevail in the lower Martian thermosphere (about 130–160 K) than the standard value, which applies to temperatures of 200–400 K. We have also modeled the escape fluxes of N from the Martian atmosphere due to photodissociation, photodissociative ionization, and electron impact dissociative ionization of N_2 , ion-molecule reactions, and dissociative recombination of N_2^+ . The magnitudes of the latter two sources depend strongly on the N_2^+ density profile, for which there are no in situ measurements. The revised ionospheric model, which incorporates the larger electron temperatures recently derived from Viking measurements (Hanson and Mantas, 1988) and a loss process for ions at high altitudes (Shinagawa and Cravens, 1989), differs substantially from those of previous models (Fox and Dalgarno, 1979; 1983; Fox, 1989). In dissociative recombination of N_2^+ , sufficient energy for escape is available only when the products are $N(^4S) + N(^2D)$, and the results are therefore sensitive to assumptions made about the product yields. Unfortunately, the experimental values for the yields of excited states of N in dissociative recombination (Queffelec et al., 1985) differ significantly from those obtained in recent ab initio calculations (Guberman, 1991). When the theoretical data are employed, the computed isotope ratio enhancement and the initial column density obtained are about 2.6 and $1.0 \times 10^{23} \text{ cm}^{-2}$, respectively. The existence of a dense early atmosphere is consistent with this model. If the initial CO_2 pressure is assumed to be 2 bars, exponential loss of the atmosphere with a time constant of about $2.2 \times 10^{16} \text{ s}$ (7×10^8 years) reproduces the measured isotope ratio.

1. INTRODUCTION

It has been more than 16 years since the mass spectrometers on the Viking landers measured the densities of neutral species and by inference the neutral temperatures in the Martian thermosphere [Nier and McElroy, 1976, 1977], and the retarding potential analyzer (RPA) measured the ion temperatures and the density profiles of the major ions [Hanson et al., 1977]. The N_2 mixing ratio was established as about 2.5% for a homopause near 120 km, and NO densities were also reported for a few altitudes below about 150 km. Thus it became possible, within the limits of the molecular data available, to model the production rates and densities of odd nitrogen species, constrained by the measured NO densities. McElroy et al. [1976] attempted to model the NO densities, but found that they could obtain agreement only if the standard cross sections for electron impact dissociation of N_2 [Winters, 1966] were increased by a factor of 5 below 40 eV. Later studies by Zipf and McLaughlin [1978] showed that the Winters cross sections were fairly accurate. Yung et al. [1977] constructed several models of nitrogen-containing species in the Martian atmosphere from the surface to 200 km. The emphasis in this study was on the odd-nitrogen compounds to be expected in the lower atmosphere. The NO densities computed by Yung et al. at thermospheric altitudes were substantially less than the Viking measured values for all of their models. Much of the data required to model the odd nitrogen species in the thermosphere was, however, not available at that time, and

many of the rate coefficients have been revised since then. In the terrestrial atmosphere, ionospheric reactions are also an important source of N atoms, but for Mars, the densities of only three of the most important ions (O_2^+ , CO_2^+ , and O^+) over a limited altitude range could be inferred from the RPA data. A complete ionospheric model was not available, although McElroy et al. [1976] and Hanson et al. [1977] modeled the density profiles of the major ions. Fox and Dalgarno [1979] presented a photochemical equilibrium model of several ions, but there was considerable uncertainty in the N_2^+ densities. In the terrestrial ionosphere, charge transfer from $O^+(^2D)$ is known to be a major source of N_2^+ [Oppenheimer et al., 1976; see also Torr and Torr, 1982], but insufficient data were available to enable the $O^+(^2D)$ densities on Mars to be confidently modeled. Fox and Dalgarno [1980] discussed the production of N atoms and presented a preliminary photochemical equilibrium model calculation of the $N(^2D)$ density profile.

The wealth of data returned from the ion and neutral spectrometers on the Pioneer Venus spacecraft [e.g., Niemann et al., 1980; Taylor et al., 1980] has, however, made possible a more complete understanding of ion and neutral chemistry in CO_2 upper atmospheres [e.g., Nagy et al., 1980; Fox, 1982a,b; Gerard et al., 1988; Bougher et al., 1990]. Fox and Dalgarno [1983] presented a model of the Martian ionosphere that included transport of neutrals by diffusion and eddy diffusion and transport of ions by ambipolar diffusion. The NO densities measured by Viking [Nier and McElroy, 1976] were adopted in their model. Some uncertainty in the ionospheric profiles remained because of the unavailability of or controversy about some important rate coefficients for reactions involved in the odd-nitrogen chemistry, including the dissociative recombination of NO^+ and the reaction of

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$O^+(^2D)$ with CO_2 . The latter reaction is important in determining the density profile of $O^+(^2D)$ and thus the source of N_2^+ due to charge transfer from $O^+(^2D)$ to N_2 . In addition, there were no data available concerning the yields of $N(^4S)$ and $N(^2D)$ in dissociative recombination of N_2^+ . Since then, discrepancies in the temperature dependence of the NO^+ dissociative recombination coefficient have been resolved [Dulaney et al., 1987; Davidson and Hobson, 1987; Johnsen, 1987], and the rate coefficient for reaction of a mixture of $O^+(^2D)$ and $O^+(^2P)$ with CO_2 has been measured [Viggiano et al., 1990]. New, but conflicting information has been obtained about the yields of $N(^4S)$ and $N(^2D)$ in dissociative recombination of N_2^+ [Queffelec et al., 1985; Guberman, 1991].

When the Viking landers descended through the atmosphere, the mass spectrometers measured an anomalous $^{15}N:^{14}N$ ratio of 0.0060, about 1.62 times the terrestrial value of 0.00368 [Nier et al., 1976; Nier and McElroy, 1977]. This enhancement presumably results from differential escape of ^{15}N , the mixing ratio of which is reduced at the exobase (about 200 km) compared to that in the bulk atmosphere, because of diffusive separation above the homopause, which is located at about 120 km. The escape of N from the Martian atmosphere is nonthermal and potential escape mechanisms include photodissociation of N_2 , which was first suggested by Brinkmann [1971], photodissociative ionization and electron impact dissociative ionization of N_2 , a few ion-molecule reactions, and dissociative recombination of N_2^+ . The first post-Viking study of nitrogen escape from Mars was carried out by McElroy et al. [1977], who found dissociative recombination to be the most important source of energetic nitrogen atoms at the Martian exobase, as did Fox and Dalgarno [1980, 1983], in later investigations. Fox and Dalgarno [1983] computed the vibrational distribution of N_2^+ at the Martian exobase and showed that vibrational excitation of N_2^+ affects the isotope separation effect that is inherent in the dissociative recombination mechanism [Wallis, 1978].

Ion temperatures in the Martian ionosphere were measured by the RPA on the Viking spacecraft and reported by Hanson et al. [1977]. A smoothed version of their profile was presented by Fox and Dalgarno [1979], and we adopt that profile here. From a comparison of model and measured ion densities, Fox and Dalgarno inferred an electron temperature profile in which T_e rose to a limiting value of about 350 K at about 180 km and was lower than the ion temperatures at altitudes higher than 200 km. Chen et al. [1978] and Rohrbaugh et al. [1979] computed much larger electron temperatures, but their computed values below 200 km differed from each other by up to a factor of 4. In the later ionospheric model of Fox [1989], the electron temperatures were assumed equal to the ion temperatures. Recently, Hanson and Mantas [1988] have used the Viking RPA data to derive electron temperatures for altitudes greater than 200 km, and the reported values of 2000 to 3000 K are larger than the ion temperatures by a factor that varies from about 4 at 200 km to about 0.5 at altitudes near 300 km. Figure 1, which is taken from Hanson and Mantas [1988], shows the temperature profile that they inferred compared to the temperature profiles computed by Rohrbaugh et al. [1979] and Chen et al. [1978]. The use of high temperatures in the model produces O_2^+ densities that diverge sharply from the measured values, if a zero flux boundary condition is

imposed at the upper boundary. Shinagawa and Cravens [1989]; (see also Shinagawa and Cravens [1992]) constructed a one-dimensional magnetohydrodynamic model of the Martian ionosphere, with which they sought to examine the interaction of the solar wind with the atmosphere and to determine if there was evidence in the ion density profiles for the existence of an intrinsic magnetic field. They found that the model ion profiles best fit the data if no intrinsic magnetic field was assumed and if some ion loss process were imposed at high altitudes. They proposed that this loss was due to the divergence of the horizontal fluxes. On Venus, similar high-altitude structure in the electron density profiles is observed when the solar wind dynamic pressure exceeds the thermal pressure of the ionosphere [Luhmann et al., 1987].

In summary, this model for odd-nitrogen and nitrogen escape incorporates updated neutral and ionospheric chemistry, higher electron temperatures and an upward ion flux boundary condition at the top of the atmosphere. Recent information about the yields of excited states in dissociative recombination is also incorporated. We show that the resulting N_2^+ profiles and/or dissociative recombination rate differ markedly from those previously reported [Fox and Dalgarno, 1983; Fox, 1989], and the isotope separation effect is greater. Although considerable uncertainties about the N_2^+

Fig. 1. Altitude profiles of the ion (T_i), electron (T_{e1}), and neutral (T_N) temperatures in the Martian thermosphere. The ion temperatures shown are those measured by the Viking RPA and reported by Hanson et al. [1977]. The curves labeled T_{e2} and T_{e3} are the temperatures associated with more energetic electron populations derived from the Viking RPA data and identified as photoelectrons and electrons of solar wind origin by Hanson and Mantas [1988]. The curves labeled T_e and T_c are the electron temperature profiles computed by Rohrbaugh et al. [1979] and Chen et al. [1978]. Taken from Hanson and Mantas [1988].

profile remain, it appears that a dense early atmosphere is required to suppress the escape of N and the efficient isotope separation that ensues.

2. THE MODEL

The thermosphere of Mars is composed mostly of CO₂, with small amounts of N₂, O, CO, Ar, O₂, and NO. The model thermosphere used here is essentially the same as that employed by Fox and Dalgarno [1979], which is based on the neutral mass spectrometer measurements of Viking 1 [McElroy et al., 1976]. The coupled continuity and flux equations were solved for 12 ions, including CO₂⁺, Ar⁺, N₂⁺, O⁺(⁴S), O⁺(²D), O⁺(²P), C⁺, N⁺, CO⁺, O₂⁺, NO⁺, O⁺⁺, and five neutral species, including NO, N(⁴S), N(²D), N(²P), and C [cf. Fox, 1982a,b, 1989]. The lower boundary conditions are photochemical equilibrium for all species except N(⁴S) and NO, for which the logarithmic derivative was fixed. This will be discussed further in section 4. At the upper boundary, diffusive equilibrium was assumed for the neutrals; for the ions of interest, upward flux boundary conditions were imposed, which will be discussed further in section 3. The eddy diffusion coefficient was assumed to be given by the expression $1.8 \times 10^{13}/M^{0.5} \text{ cm}^2 \text{ s}^{-1}$, where M is the total number density of neutrals in cm^{-3} , which has been found to give a fairly good fit to the values presented by Nier and McElroy [1977] and which is similar to the expression derived from Pioneer Venus data for the thermosphere of Venus [von Zahn et al., 1980]. The solar fluxes adopted for high and low solar activity were taken from the F79050N and SC#21REFW spectra, respectively, of H. Hinteregger (private communication, 1979) [cf. Torr et al., 1979]. The interaction of energetic electrons with nitrogen gas has been modeled by Fox and Victor [1988], who used cross sections for electron impact excitation, ionization and dissociation of N₂ from Ajello and Shemansky [1985], Cartwright et al. [1977] (see also Trajmar et al. [1983]), Rapp and Englander-Golden [1965], Crowe and McConkey [1973], and Zipf and McLaughlin [1978] (see also Zipf [1984]). The cross sections for electron impact excitation and ionization of N₂ used here are the same as those employed by Fox and Victor.

We have constructed a new model of the Martian ionosphere that takes into account the high electron temperatures, and loss of ions from the top of the ionosphere. The assumed temperatures profiles are shown in Figure 2. The neutral temperature profile is the same as that constructed by Fox and Dalgarno [1979] to fit the neutral density profiles measured by Viking 1 and is given by the expression $T_n = 225 - 95 \exp[(100 - z)/70]$. The ion temperature is a smoothed version of the ion temperature profile measured by the RPA on Viking 1, as presented by Hanson et al. [1977]. The assumed electron temperature profile is given by

$$\begin{aligned} T_e &= T_n; & z < 130 \text{ km} \\ T_e &= 700 - 536 \exp[(130 - z)/65.4]; & 130 < z < 180 \text{ km} \\ T_e &= 4200 - 3750 \exp[(180 - z)/89.6]; & z > 180 \text{ km}, \end{aligned} \quad (1)$$

which is similar to that calculated by Rohrbaugh et al. [1979] (see Figure 1). We chose the profile of Rohrbaugh et al. in preference to that of Chen et al. [1978] because we found that the observed O₂⁺ density profile could be better fitted below 200 km with these values.

Fig. 2. Ion (T_i), electron (T_e), and neutral (T_n) temperatures adopted in this model. The neutral temperature profile is that constructed by Fox and Dalgarno [1979] to fit the measured neutral densities measured by Viking 1. The ion temperature profile is a smoothed version of the ion temperatures measured by the RPA on Viking 1, and the electron temperature profile was constructed to approximate the values computed by Rohrbaugh et al. [1979].

3. MOLECULAR DATA

The major sources of odd nitrogen are photodissociation and electron impact dissociation of N₂. There is little information available about the yields of the excited ²D and ²P electronic states of N in photodissociation of N₂. In this work, as in previous models, we have assumed that every time a channel becomes energetically allowed, the yield for that channel goes to 1. While this may not be strictly correct, the result obtained for solar photodissociation at small optical depths is that about 55% of the N atoms are produced in excited states, 32% in ²D and 23% in ²P. This is similar to the common assumption that 50% of the N atoms are produced in the ²D state and 50% in the ⁴S state [e.g., Rusch et al., 1991]. Since loss of N(²P) is mostly by radiation (and quenching) to N(²D), the assumptions are equivalent for all practical purposes.

The rate coefficients for ion-molecule and neutral-neutral reactions that are important to the production and loss of nitrogen atoms and other odd nitrogen species (NO, NO⁺, N⁺) and those ionospheric reactions that have been updated since the models of Fox [1982a,b] and Fox and Dalgarno [1983] are shown in Table 1. Dissociative recombination of N₂⁺ (reaction (R1) in Table 1)

is an important source of nitrogen atoms. The uncertainty in the N₂⁺ densities that existed in previous studies due to

TABLE 1. Rate Coefficients for Reactions Involving Odd Nitrogen and Nitrogen Escape in the Martian Atmosphere and Other Rate Coefficients That Have Been Updated Since the Models of Fox [1982a,b] and Fox and Dalgarno [1983]

No.	Reaction	Rate Coefficient, $\text{cm}^3 \text{s}^{-1}$	References
(R1)	$\text{N}_2^+ + e \rightarrow \text{N} + \text{N}$	$2.2(-7)^a (300/T_e)^{0.39}$	Zipf [1980]
(R2)	$\text{NO}^+ + e \rightarrow \text{N} + \text{O}$	$4.3(-7)(300/T_e)^{0.7}$	Davidson and Hobson [1987]
		76% $\text{N}(^2D)$; 24% $\text{N}(^4S)$	Kley et al. [1977]
(R3)	$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	$1.4(-10)^a (300/T_i)^{0.44}$	McFarland et al. [1974]
(R4)	$\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$	$1.2(-12)(300/T_i)^{0.41}$	Burley et al. [1987]
		$T_i < 1625 \text{ K};$ $6.0(-13)(T_i/1625)^{2.25}$ $T_i > 1625 \text{ K}$	
(R5)	$\text{N}^+ + \text{CO} \rightarrow \text{N} + \text{CO}^+$	$5.9(-10)$	Miller et al. [1984]
(R6)	$\text{O}^{++} + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{O}^+$	$\leq 1.6(-9)^b$	Howorka et al. [1979]
(R7)	$\text{O}^+(^2D) + \text{N}_2 \rightarrow \text{N}_2^+ + \text{O}$	$8(-10)$	Johnsen and Biondi [1980]
(R8)	$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	$4.8(-10)$	Smith et al. [1978]
(R9)	$\text{N}^+ + \text{CO}_2 \rightarrow \text{CO}^+ + \text{NO}$	$2.5(-10)$	Smith et al. [1978]
(R10)	$\text{N}^+ + \text{O}_2 \rightarrow \text{N} + \text{O}_2^+$	$3.1(-10)$	Smith et al. [1983]
		30% $\text{N}(^2D)$; 70% $\text{N}(^4S)$	O'Keefe et al. [1986]
(R11)	$\text{O}_2^+ + \text{N}(^2D) \rightarrow \text{O}_2 + \text{N}^+$	$9.3(-11)$	(reverse of (R10))
(R12)	$\text{O}^+(^2P) + \text{N}_2 \rightarrow \text{N}_2^+ + \text{O}$	$4.8(-10)$	Lavollée and Henri [1989]
(R13)	$\text{O}^+(^2D, ^2P) + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{O}$	$1.0(-9)$	Viggiano et al. [1990]
	$\rightarrow \text{CO} + \text{O}_2^+$	$6.0(-11)$	
(R14)	$\text{CO}^+ + e \rightarrow \text{C} + \text{O}$	$1(-7)(300/T_e)^{0.48}$	Mitchell and Hus [1985] see also Mitchell [1990]
(R15)	$\text{N}(^2D) + \text{O} \rightarrow \text{N}(^4S) + \text{O}$	$6.9(-13)$	Fell et al. [1990]
(R16)	$\text{N}(^2D) + \text{CO}_2 \rightarrow \text{NO} + \text{CO}$	$3.5(-13)$	Piper et al. [1987]
(R17)	$\text{N}(^2D) + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$6.9(-11)$	Fell et al. [1990]
(R18)	$\text{N}(^2D) + e \rightarrow \text{N}(^4S) + e$	$3.8(-12)T_e^{0.81}$	Berrington and Burke [1981]
(R19)	$\text{N}(^4S) + \text{NO} \rightarrow \text{N}_2 + \text{O}$	3.4×10^{-11} see text	DeMore et al. [1992]

^a Read as 2.2×10^{-7} .^b The rate coefficient for this reactions is an upper limit. The products are unknown, but the dissociative channel probably dominates.

the unknown rate coefficient for reaction of $\text{O}^+(^2D)$ with CO_2 has now been largely resolved by the work of Viggiano et al. [1990], who measured the rate coefficient for reaction of a mixture of $\text{O}^+(^2D)$ and $\text{O}^+(^2P)$ with CO_2 ; they reported that the total rate coefficient is about $1.06 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$, with the major product channel being $\text{CO}_2^+ + \text{O}$.

The rate coefficient adopted here for the dissociative recombination of N_2^+ is that reported by Zipf [1980]: $2.2 \times 10^{-7}(300/T_e)^{0.39} \text{ cm}^3 \text{s}^{-1}$. The value used in previous models, $3.5 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ at 300 K [Fox and Dalgarno, 1979, 1980, 1983; Fox, 1982] was that measured by Mul and McGowan [1979]; it is one of those subject to a downward revision by a factor of 2 due to an error in the data analysis that applies to all merged beam measurements reported by the University of Western Ontario group prior to 1985 [Noren et al., 1989; Mitchell, 1990]. (The rate coefficient for dissociative recombination of CO^+ reaction (R14) is also among those so revised.) Noren et al. [1989] have recently measured the cross sections for dissociative recombination of N_2^+ in the ground vibrational state and derived a rate coefficient of $3.6 \times 10^{-8} \text{ cm}^3 \text{s}^{-1}$ at 300 K, which is about a factor of 5 lower than the previously accepted values. Prior measurements of the dissociative recombination coefficient of N_2^+ include the shock tube measurements of Cunningham and Hobson [1972], who reported values that exhibited a temperature dependence of $T_e^{-0.37}$ and extrapolated to $1.78 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ at 300 K, and those of Mehr and Biondi [1969], who performed a microwave afterglow experiment

that indicated a similar $T_e^{-0.39}$ temperature dependence and a 300 K value of $1.8 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$. Measurements and calculations subsequent to the Noren et al. study have tended to support these earlier measurements. The flowing afterglow/Langmuir probe experiment of Canosa et al. [1991] indicated that dissociative recombination from $v = 0$ of N_2^+ proceeds with a 300 K rate coefficient of $2.6 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$. Guberman [1991] has performed large ab initio calculations of dissociative recombination of $\text{N}_2^+(v = 0)$ and has reported a rate coefficient of $1.6 \times 10^{-7}(300/T_e)^{0.37} \text{ cm}^3 \text{s}^{-1}$. Since about 40% of the $\text{N}_2^+(v)$ ions above the exobase in our model are vibrationally excited, the rate coefficient for ground state N_2^+ is not entirely appropriate. The value reported by Zipf [1980] applies to an N_2^+ plasma with a vibrational temperature of about 1500 K [Johnsen, 1987]. Bates and Mitchell [1991] reanalyzed the data of Zipf [1980] and reported a rate coefficient of $2.6 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ at 300 K for dissociative recombination from the ground state of N_2^+ . Furthermore, they concluded also that the rate coefficients for dissociative recombination of N_2^+ in the first two vibrationally excited levels were smaller, but they could not derive numerical values. We adopt the rate coefficient of Zipf as our standard value, but we consider the consequences for the model if the rate coefficient is smaller by about 25%, closer to the value measured in the microwave afterglow and shock tube studies, and that computed by Guberman [1991].

Dissociative recombination of N_2^+ may proceed in the following channels:

This reaction is thus potentially an important source of electronically excited nitrogen atoms, the magnitude of which depends on the branching ratios into the above channels. The experiments of *Queffelec et al.* [1985] suggested that the predominant channel is (R1b), with an upper limit of 10% of the reactions proceeding according to (R1a). The calculations of *Guberman* [1991] indicate, however, that in dissociative recombination of $N_2^+(v=0)$ the majority of the recombinations, about 88%, produce $N(^4S) + N(^2D)$ (channel R1a). *Guberman* has suggested that the yield may vary substantially with the vibrational level of the ion and that the results of *Queffelec et al.* [1985] may be appropriate to vibrationally excited states.

The ionospherically important reaction (R4)

has been found to have a negative temperature dependence at low energies and a positive temperature dependence at high energies. We have fitted the data presented by *Burley et al.* [1987] with the two expressions presented in Table 1 for the temperature regions $T_i < 1625$ and $T_i > 1625$. Reaction (R3) produces an $N(^2D)$ at least 90% of the time [*Frederick and Rusch*, 1977] and we assume here that the yields are 90% $N(^2D)$ and 10% $N(^4S)$. Although the rate coefficient for reaction of O^{++} with N_2 (reaction (R6)) has been measured, the products are unknown. Because of the large exothermicity, we assume that the dissociative channel dominates.

The rate coefficient for reaction (R10)

is well established, but the distributions of the electronic states of the product N atoms has been measured only recently by *O'Keefe et al.* [1986], who reported that 30% of the N atoms are produced in the 2D state and 70% in the 4S state. Although this reaction is of minor importance in the Martian ionosphere, where the O_2 densities are small, the reverse reaction for the nearly thermoneutral channel in which $N(^2D)$ is produced is potentially important. The measurement of the $N(^2D)$ yield in reaction (R10) makes it possible to derive a rate coefficient for reaction (R11) [*Dalgarno*, 1970].

The major loss processes for $N(^2D)$ include quenching by atomic oxygen (R15), and reaction with CO_2 (R16). The rate coefficient for reaction (R15) has been the subject of much controversy in recent years, since the measurement of *Jusinski et al.* [1988] showed the reaction to proceed at rates that were 20–40 times the previously accepted values. Subsequently, however, measurements of *Piper* [1989] and *Fell et al.* [1990] have yielded rate coefficients near the previous values. We adopt the value $6.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ reported by *Fell et al.*, as well as their rate coefficient for reaction of $N(^2D)$ with NO (reaction (R17)). The rate coefficient for reaction (R16)

was taken from the measurements of *Piper et al.* [1987] and is slightly larger than the value recommended by *Schofield* [1979]. Although the $N(^2D)$ density profile is reduced by

the adoption of this rate coefficient, the source of NO due to this reaction is not greatly affected because reaction (R16) is the major loss process for $N(^2D)$ over all altitudes below about 180 km.

The density profiles of the major ions obtained in our low and high solar activity model calculations are shown in Figures 3a and 3b, where the low solar activity profiles are compared to those measured by the RPA on Viking [*Hanson et al.*, 1977]. We found, as did *Shinagawa and Cravens* [1989], that using the high electron temperatures, the O_2^+ profile can only be reproduced by assuming a loss process for ions at the top of the ionosphere. Therefore, we imposed an upward flux boundary condition at the top of the model, 395 km and found that an O_2^+ flux of $4.75 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ best reproduces the measured O_2^+ densities. The short-dashed line in Figure 3a shows the O_2^+ profile obtained with a zero-flux boundary condition and high electron temperatures; it clearly illustrates that the measured densities cannot be reproduced within this model. The fluxes of the other major ions are chosen so that the ratios of their fluxes to that of O_2^+ are approximately equal to the ratio of the densities at the upper boundary of the model. Equivalently, the ion velocities are assumed to be equal, with a value of about 0.91 km s^{-1} . This seems to be a reasonable assumption, since the minor ions are probably entrained in the flow of the major ion, O_2^+ . The resulting fluxes of CO_2^+ , N_2^+ , O^+ , and NO^+ in the low solar activity model are given in Table 2. The agreement between the measured and model O^+ density profiles lends some support to this procedure. There are no in situ measured densities at high solar activity, and we have somewhat arbitrarily assumed that the upward velocities (0.88 km s^{-1}) are close to those of the low solar activity model. We were, however, unable to impose upward velocities as large as those of the low solar activity model, probably because the higher ion densities reduce the diffusion coefficients in the high solar activity model. This would seem to indicate that the upward fluxes we have imposed, which are also shown in Table 2, are close to their limiting values.

4. ODD NITROGEN DENSITIES

Altitude profiles of the densities of NO, $N(^4S)$, $N(^2D)$, and $N(^2P)$ are presented in Figure 4, along with the measured values for NO from Viking 1 [*Nier and McElroy*, 1976]. Because of the location of the lower boundary at 100 km in our model, it is necessary to allow for downward fluxes of $N(^4S)$ and NO, which are lost partly by transport to lower altitudes. While we have imposed photochemical equilibrium lower boundary conditions on the ions and zero-flux boundary conditions on $N(^2D)$ and $N(^2P)$, for $N(^4S)$ and NO, we have required that the logarithmic derivatives of the density profiles at 100 km equal those in the model of *Yung et al.* [1977], in which the lower boundary was at 60 km. Experimentation with different boundary conditions showed that the NO densities below 120 km are sensitive to the choice of boundary conditions and therefore are of limited validity, but densities at 130 km and above are relatively unaffected. At 130 km, chemical production and loss of NO in our model differ by only 5%. Figure 4 shows that the computed NO densities above 130 km are a factor of 2–3 smaller than the measured values. This discrepancy cannot be resolved by changes in any of the reactions that interconvert odd nitrogen species or in the yields of electronic states

Fig. 3a. Computed profiles of some of the major ions in the Martian ionosphere for the low solar activity model. The long-dashed curved are values reported by *Hanson et al.* [1977] from the Viking 1 RPA data. The short-dashed curves are the O_2^+ and N_2^+ profiles computed with a zero-flux boundary condition. In this model, the O_2^+ densities diverge sharply from the measured values above about 180 km.

Fig. 3b. Computed profiles of some of the major ions in the Martian ionosphere for the high solar activity model.

of N in the atomic-nitrogen producing reactions, since even the total odd nitrogen densities ($N(^4S) + N(^2D) + N(^2P) + NO$) in the model are significantly less than the measured NO densities. It is necessary therefore to conclude that either the total production rate of odd nitrogen is underestimated in the model or the loss rate is overestimated.

The major sources of odd nitrogen are photodissociation, electron impact dissociation and dissociative ionization of N_2 , and a few ionospheric reactions shown in Table 1: dissociative recombination of N_2^+ (reaction (R1)), and the ion-molecule reactions (R3), (R4), and (R6). Our model shows that the source due to ion-molecule reactions is small, so uncertainties in those rate coefficients or in the model ion densities will not have a significant effect on the odd-nitrogen production rates. McElroy *et al.* [1976] obtained agreement between the measured and model NO profiles by increas-

ing the cross section for electron impact dissociation of N_2 measured by Winters [1966] by a factor of 5 for energies less than 40 eV, thus increasing the source of odd nitrogen. By comparing the total cross sections for electron-impact excitation of singlet states of N_2 derived from generalized oscillator strength data to their measured emissions cross sections, Zipf and McLaughlin [1978] showed that the Winters cross sections are fairly accurate under optically thin conditions. Because discrete absorption into predissociating singlet states dominates the photodissociation cross sections from 668 to 1000 Å, the cross sections at these wavelengths show considerable structure. The N_2 absorption and ionization cross sections that we have used are those presented by Kirby *et al.* [1979], and are square-wave fits to the data of Huffman [1969], Carter [1972], and Cook and Metzger [1964]. The photodissociation cross section shortward of the ionization threshold, 796 Å, is assumed to be the difference between the photoabsorption cross section and the photoionization cross section. The potential for inaccuracy in the photodissociation cross sections is considerable, and it is possible that in order to obtain accurate N atom production rates, it will be necessary to construct high-resolution cross sections appropriate to temperatures in the Martian thermosphere, similar to the procedure that has been carried out for dissociation of CO in the Venus thermosphere by Fox and Black [1989], and dissociation of H_2 in the Jovian thermosphere by Kim and Fox [1991]. Unlike the case of H_2 on Jupiter, (but like CO on Venus), absorption in the wavelength range of interest on Mars will not be dominated by N_2 , so effects on the optical depth of solar photons will be negligible. It is possible, however, that the production rates of N atoms may be in error by up to a factor of 2 or so. Such effects should

TABLE 2. Upward Fluxes of the Major Ions Assumed at the Upper Boundary of the Model

Species	Low Solar Activity Flux, $\text{cm}^{-2} \text{s}^{-1}$	High Solar Activity Flux, $\text{cm}^{-2} \text{s}^{-1}$
O_2^+	4.75(7) ^a	6.82(7)
N_2^+	1.92(6)	5.67(6)
O^+	4.96(6)	1.63(7)
NO^+	1.96(6)	4.20(6)
CO_2^+	1.92(6)	8.88(6)

^a Read as 4.75×10^7 .

Fig. 4. Computed altitude profiles of the densities of $N(^4S)$, $N(^2D)$, $N(^2P)$, and NO in the Martian atmosphere. The dashed curves are the computed profiles for a model in which the rate coefficient for reaction (R19) of Davidson and Hanson [1990] is adopted. The squares are the measured values from Viking 1 [Nier and McElroy, 1976].

be investigated, but since photodissociation contributes less than 40% of the N atom production below 145 km, the potential impact of constructing and employing high resolution cross sections is limited.

The major loss process for odd nitrogen in the thermosphere of Mars is reaction (R19)

In our standard model we adopt the rate coefficient ($3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) recommended by *Atkinson et al.* [1989] (see also *DeMore et al.* [1992]) for temperatures from 200 to 400 K. The temperatures in the lower Martian thermosphere are, however, outside this range [*McElroy et al.*, 1976]. *Clyne and McDermid* [1975] studied the reaction in a discharge flow system and reported a value for k_{19} of $8.2 \pm 1.4 \times 10^{-11} \exp[-(410 \pm 120)\text{K}/T] \text{ cm}^3 \text{ s}^{-1}$. The positive temperature coefficient was interpreted as suggesting the presence of a small activation barrier of 820 cal/mol (0.035 eV). More recent high-temperature measurements by *Davidson and Hanson* [1990] have indicated a larger barrier of about 0.07 eV. If such an activation barrier exists, the rate coefficient may well be smaller at temperatures that prevail in the lower thermosphere of Mars than at the higher temperatures of the terrestrial middle atmosphere or lower thermosphere. In the altitude region where NO densities are reported, about 128–145 km [*Nier and McElroy*, 1976], temperatures inferred from the Viking 1 neutral mass spectrometer data range from about 120 to 180 K [*McElroy et al.*, 1976]. Temperatures derived from Viking 2 data oscillate between about 130 and 150 K over the altitude range where NO densities were reported, 115 to 137 km. The expression of *Clyne and McDermid* [1975] implies that the rate coefficient varies from 2.7×10^{-12} to $8.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ from 120 to 180 K. If we adopt the rate coefficient for reaction (R19) of *Davidson and Hanson* [1990], $7.1 \times 10^{-10} \exp(-787/T) \text{ cm}^3 \text{ s}^{-1}$, along with the smoothed temperature profile shown in Figure 2, we obtain the odd nitrogen densities given by the dashed lines in Figure 4. Substantial agreement of the computed NO densities with the measured values is obtained. The values are similar to those obtained using a temperature independent rate coefficient of $6.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, the value derived from the expression of *Clyne and McDermid* [1975] for a temperature of 160 K.

5. NITROGEN ESCAPE

Escape of nitrogen from Mars is due to several nonthermal escape mechanisms. Previous studies have established that the escape rate is significant and likely to account for the observed enhancement in the $^{15}\text{N}:^{14}\text{N}$ isotope ratio [*McElroy et al.*, 1976; *Nier et al.*, 1976; *Fox and Dalgarno*, 1980, 1983; *Fox*, 1989]. If the current escape rate of nitrogen atoms is known, the initial column density and isotope enhancement over the age of the solar system can be computed. If we call $\phi(t)$ the $^{14}\text{N}_2$ flux at time t , and N_{14} the column density of $^{14}\text{N}_2$, then the initial column density can be found by integrating

$$\frac{dN_{14}}{dt} = -\phi(t) \quad (2)$$

over the age of the solar system, 4.5 b.y. Similarly, the flux of $^{15}\text{N}^{14}\text{N}$ is given by

$$\frac{dN_{15}}{dt} = -f_e(t)\phi(t) = -Rf(t)\phi(t), \quad (3)$$

where N_{15} is the column density of $^{15}\text{N}^{14}\text{N}$ and the deficiency factor $R = f_e(t)/f_o(t)$ is the net relative escape rate of ^{15}N compared to ^{14}N [*McElroy et al.*, 1976; *Nier et al.*, 1976]. If the escape mechanisms themselves do not contribute to the isotope discrimination, then R is equal to the ratio of ^{15}N to ^{14}N at the exobase. Using eddy diffusion coefficients derived from the Viking measurements, *McElroy et al.* [1977] computed a value of 0.82 for R . The time rate of change of the isotope enhancement f is given by

$$\frac{df(t)}{dt} = \frac{\phi(t)f(t)[(1-R(t))]}{N_{14}(t)}. \quad (4)$$

[*Nier et al.*, 1976]. This equation also can be integrated backward in time, taking care to account properly for variations in the escape rates due changes in the composition of the atmosphere, the altitude of the homopause, and the altitude of the exobase.

We assumed that the homopause in the past was at the same pressure level as it is at present, consistent with the conclusion of *Leovy* [1982]. The variation of the escape mechanisms with time was computed by *Fox and Dalgarno* [1983], and their result, which we adopted here, will be briefly summarized. The escape fluxes due to photodissociation and dissociative ionization of N_2 , as well as to dissociative recombination of N_2^+ , are proportional to the mixing ratio of N_2 for small mixing ratios. As N_2 becomes the major constituent of the atmosphere, the N_2 density determines the altitude of the exobase and the escape rate reaches a limiting value. The source due to reaction (R3) is proportional to the density of O as well as to that of N_2 . As the N_2 abundance increases, the rate initially increases, but then reaches a maximum and begins to decrease as the exobase density of O decreases. Similarly, the flux due to reaction (R6) initially increases as the N_2 mixing ratio increases, but eventually loss of O^{++} is mainly by reaction with N_2 . At this point, since the density of O^{++} is inversely proportional to that of N_2 , the rate of the reaction is proportional only to the atomic oxygen density, and the escape flux decreases more strongly than that due to reaction (R3). Numerical values can be found in Figure 3 of *Fox and Dalgarno* [1983].

The escape mechanisms and the computed fluxes are presented in Table 3. The sources due to photodissociation, photodissociative ionization, and photoelectron impact dissociative ionization are the same as those presented by *Fox and Dalgarno* [1983] and *Fox* [1989]. *Prokop and Zipf* [1982] have reported that the average energy of N atoms produced in electron impact dissociation of N_2 is about 0.45 eV, significantly less than the escape energy of an N atom. Therefore, we have assumed that the escape flux due to electron impact dissociation is negligible. The sources due to dissociative recombination and ion-molecule reactions have been updated to account for changes in our ionospheric model. Dissociative recombination of N_2^+ can proceed by a number of different channels, but sufficient energy is available for escape only if the products are $\text{N}(^2D) + \text{N}(^4S)$. The exothermicity for this channel is 3.45 eV, about twice the escape energy for ^{14}N at the Martian exobase, 1.74 eV. The escape energy of ^{15}N , 1.86 eV, is more than 14/29 (the fraction of energy that the ^{15}N will depart with in dissociative recombination of $^{15}\text{N}^{14}\text{N}^+$) of the available energy, and differential escape

TABLE 3. Computed ^{14}N Escape Fluxes

Process	Escape Flux, $10^5 \text{ cm}^{-2} \text{ s}^{-1}$		
	Low SA ^a	High SA ^a	Average
$\text{N}_2 + h\nu \rightarrow \text{N} + \text{N}$	0.59	1.4	1.0
$\text{N}_2 + h\nu \rightarrow \text{N}^+ + \text{N} + \text{e}$	0.17	0.60	0.39
$\text{N}_2 + \text{e} \rightarrow \text{N}^+ + \text{N} + 2\text{e}$	0.14	0.48	0.31
$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	0.49	1.40	0.95
$\text{O}^{++} + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{O}^+$	0.059	0.17	0.11
$\text{N}_2^+ + \text{e} \rightarrow \text{N} + \text{N}$	0.58	3.5	2.0
Total	2.0	7.5	4.8

^a Solar activity.

Fig. 5. N_2^+ vibrational distribution computed for the low solar activity model of the Martian ionosphere. The model is essentially the same as that described by Fox and Dalgarno [1983].

of ^{14}N and ^{15}N occurs if the N_2^+ is in the ground vibrational state. A detailed calculation by Wallis [1978] showed that the escape probability for an ^{14}N released in dissociative recombination of N_2^+ in the ground vibrational level is 41.6% and that for ^{15}N is 23.7%. If the N_2^+ is vibrationally excited, 0.27 eV is added to the exothermicity for every quantum of excitation and the isotope discrimination is diminished considerably.

In order to compute the isotope fractionation rate, we have computed the vibrational distribution of N_2^+ in the Martian ionosphere using an updated version of the model of Fox and Dalgarno [1983], which is similar to the terrestrial model of Fox and Dalgarno [1985]. The most important process in determining the vibrational distribution of N_2^+ near the exobase (200 km) is fluorescent scattering of solar radiation in the first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and Meinel

($A^2\Pi_u \rightarrow X^2\Sigma_g^+$) bands. The computed distribution, presented in Figure 5, shows that at low altitudes quenching is effective in limiting the fraction vibrationally excited to 20%, but at higher altitudes the fraction vibrationally excited increases to 43% near 200 km. Although the vibrational distribution was computed assuming photochemical equilibrium, the distribution is nearly constant above the altitudes where photochemical equilibrium breaks down, about 220 km. Thus the N_2^+ ions at those altitudes that are transported from nearby regions will have the same vibrational distribution as those produced locally. The fractions in the first six vibrational levels at the Martian exobase, near 200 km, are given in Table 4.

The isotope fractionation is highly dependent on the number of dissociative recombinations assumed to proceed via the $\text{N}(^4S) + \text{N}(^2D)$ channel, reaction (R1a). Fox and Dal-

garno [1983] assumed that the channels were produced in a statistical distribution, which would imply that 24% of the dissociative recombinations produce $N(^4S) + N(^2D)$. The predicted isotope enhancement over the terrestrial value in this model was more than 2.5, from which it was inferred that the escape rate had been reduced in the past, possibly by the presence of a dense, early atmosphere. Later experiments on the dissociative recombination of N_2^+ by Queffelec *et al.* [1985] suggested, however, that the major product channel is $N(^2D) + N(^2D)$, for which the exothermicity is only 1.06 eV, much less than necessary for escape of N. They placed an upper limit of 10% on the fraction of dissociative recombinations proceeding by the $N(^4S) + N(^2D)$ channel. Calculations based on the yields reported by Queffelec *et al.* [1985] for an earlier Martian ionosphere model with lower electron temperatures and a zero flux upper ion boundary condition [Fox, 1989] gave initial isotope ratios of 1.7–2.0 and initial column densities of about $(5.7 - 8.5) \times 10^{22} \text{ cm}^{-2}$.

Recently, Guberman [1991] has carried out *ab initio* calculations that show that the major channel for dissociative

recombination of N_2^+ in the ground vibrational state is the $N(^4S) + N(^2D)$ channel, with a yield of 0.88, significantly larger even than that assumed by Fox and Dalgarno [1983], and much larger than indicated by the experiments of Queffelec *et al.* [1985]. Guberman noted that the yield of $N(^2D) + N(^2D)$ may be larger for dissociative recombination from vibrationally excited N_2^+ . In this work we have used the yield suggested by Guberman for dissociative recombination from ground state N_2^+ and that of Queffelec *et al.* for N_2^+ in vibrationally excited states. The computed isotope enhancement ratio as a function of time before present is shown in Figure 6, and the column density of N_2 is shown in Figure 7. We find that the total N escape rate is only slightly larger but the $^{15}\text{N}:^{14}\text{N}$ isotope fractionation is significantly more effective than that of the model based on the Queffelec *et al.* yields [Fox, 1989]. The predicted isotope enhancement after 4.5 b.y. is about 2.6, considerably larger than the observed value, which is achieved in only 1.4×10^9 years.

This result is superficially similar to that obtained by Fox and Dalgarno [1983] because of a cancellation of effects: the dissociative recombination rate is smaller, but the escape efficiency is larger due to the adoption of the yields of Guberman. The N_2^+ profile itself is similar to that presented by Fox and Dalgarno [1983], largely because the major loss processes for N_2 over most of the exosphere are the reactions with CO_2 and O. Dissociative recombination becomes important in this model only near 300 km. Previously, it was assumed that low electron temperatures caused efficient loss of O_2^+ and other molecular ions by dissociative recombination, but now an ion loss process is imposed at the upper boundary. If an early atmosphere with an initial CO_2 pressure of 2 bars is assumed, exponential loss of the atmosphere

TABLE 4. Vibration Distribution of N_2^+ at the Martian Exobase (200 km)

v	Fraction
0	0.573
1	0.208
2	0.105
3	0.056
4	0.0326
5	0.0256

Fig. 6. Isotope enhancement ratio relative to the terrestrial value that is predicted to occur during the time indicated before the present. In the calculation the escape rate and isotope differentiation rate are derived by integrating backward in time, taking into account changes in the composition of the atmosphere, the height of the exobase and the homopause. The solid curve is for no suppression of escape over the age of the solar system. The dashed curve is for an initial atmosphere of 2 bars of CO_2 that is lost exponentially with a time constant of about 700 m.y.

Fig. 7. N_2 column density as a function of time before the present. The calculations are as described in the caption for Figure 6, and the solid and dashed curves are for the same cases.

with a time constant of 2.2×10^{16} s, about 700 m.y., gives the observed isotope enhancement ratio of 1.62 and an initial N_2 column density of 2.6×10^{22} cm^{-2} . The isotope enhancement ratio and the initial column density as a function of time for this case are represented by the dashed curves in Figures 6 and 7. An initial CO_2 pressure of 1 bar yields the measured value for the isotope ratio if the time constant for loss is 2.6×10^{16} s (840 m.y.) Observations of branching valley networks on the surface of Mars have been interpreted as showing that liquid water was present early in the history of the planet, and therefore the early atmosphere must have been warm and dense. Analyses suggest that such an atmosphere would, however, have been unstable, since CO_2 would have been rapidly deposited as carbonates in the presence of liquid water [e.g., Pollack et al., 1987; Carr, 1989; McKay and Stoker, 1989].

If the experimental upper limit for the yield of channel (R1a) derived by Queffelec et al. [1985] is used for dissociative recombination of both ground state and vibrationally excited N_2^+ in the revised ionospheric model, the predicted isotope enhancement ratio is 1.63, nearly equal to the measured value; the initial column density of N_2 would be about 5.7×10^{22} cm^{-2} . This model would not allow for the presence of a dense initial atmosphere unless it was lost extremely rapidly.

6. EFFECT OF UNCERTAINTIES IN THE IONOSPHERIC MODEL

The source due to dissociative recombination of N_2^+ depends critically on the model N_2^+ densities, which have not been measured in situ by any spacecraft, and on the value adopted for the dissociative recombination coefficient. The major production mechanisms for N_2^+ are photoionization and electron impact ionization of N_2 , the cross sections for

which are relatively well known. About a third of the N_2^+ at the exobase is, however, produced by charge transfer from $\text{O}^+(^2D)$. Although the rate coefficient for the reaction is fairly well defined, having been measured and found to be nearly gas kinetic by Johnsen and Biondi [1980] and Rowe et al. [1980], the densities of $\text{O}^+(^2D)$ are still somewhat uncertain but are obtained self-consistently in the models. The major mechanism for loss of $\text{O}^+(^2D)$ is reaction with CO_2 , the rate coefficient for which has recently been measured by Viggiano et al. [1990], as mentioned above. But the rate for quenching of $\text{O}^+(^2D)$ by O has not been measured. In our standard model, we assume a rate coefficient of 1×10^{-11} $\text{cm}^3 \text{s}^{-1}$, as suggested by Orsini et al. [1977] from an analysis of Atmosphere Explorer data. A value of 1×10^{-10} was suggested by Oppenheimer et al. [1976]. The use of the larger value, however, reduces the N_2^+ densities at the exobase (and therefore the dissociative recombination rate) by only about 5%. Even with this larger rate, loss of $\text{O}^+(^2D)$ by reaction with CO_2 is still much faster than quenching by O.

The major loss mechanism for N_2^+ at the Martian exobase is charge transfer to CO_2 , which proceeds with a nearly gas kinetic rate coefficient of 7.7×10^{-10} $\text{cm}^3 \text{s}^{-1}$ [Smith et al., 1978]. Since dissociative recombination is not as important in determining the densities of N_2^+ at the exobase, a reduction in the dissociative recombination coefficient also reduces the computed escape rate. If the dissociative recombination coefficient for N_2^+ that is appropriate to the vibrational distribution that exists at the Martian exobase is closer to the values $1.6 - 1.8 \times 10^{-7}$ $\text{cm}^3 \text{s}^{-1}$ that were measured in the early shock tube and microwave afterglow experiments [Cunningham and Hobson, 1972; Mehr and Biondi, 1969] and obtained in the calculation of Guberman [1991] for the ground vibrational level, then the escape flux due to dissociative recombination will be reduced by less than 25%. For this case, the predicted isotope enhancement ratio is found

to decrease by about 10% to a value of 2.34. Thus, although the isotope enhancement effect is smaller, this case also requires some suppression of the escape over time, such as that supplied by a dense early atmosphere.

The behavior of the rate coefficient with electron temperature is also important. In our first models [Fox and Dalgarno, 1980, 1983], we assumed an electron temperature profile that was lower at altitudes above 200 km than the ion temperatures measured by the Viking spacecraft. The resulting dissociative recombination rates were larger and were assumed to be responsible for the rapid falloff of the O_2^+ and electron densities at high altitudes. Changes in the rate coefficients and the addition of transport to the model allowed the electron temperatures to be increased to values equal to the ion temperatures [Fox, 1989]. The recent report of Hanson and Mantas [1988] has shown that the electron temperatures were very large and comparable to those computed by Rohrbaugh et al. [1979] and Chen et al. [1978], at least above 200 km. In this model we adopt a similar T_e profile to that computed by Rohrbaugh et al. [1979]. Our electron temperatures are still somewhat smaller than those computed by Chen et al. [1978] but by a factor of 50% or less over most of the altitude range from 200 to 300 km. If the electron temperature in the model is increased by 50% above 200 km, the dissociative recombination rate decreases by about 15%. For this case, the predicted isotope enhancement ratio decreases to about 2.47, so some suppression of escape is still required.

In addition to these uncertainties in the model parameters, there is also some uncertainty in the mode of transport assumed to be responsible for the loss of ions at the top of the ionosphere. We have assumed here that the upward transport of plasma is by ambipolar diffusion. It is possible that this transport process is MHD drift, due to the role of intrinsic or solar wind induced magnetic fields [Shinagawa and Cravens, 1989, 1992]. If the atmosphere was denser in the past, the interaction with the solar wind might have been different, resulting in different ion and electron temperatures and ion density profiles.

7. CONCLUSIONS

We have constructed a revised thermosphere-ionosphere model that incorporates new information on Martian electron temperatures, ion-molecule rate coefficients, and a loss process for ions at the top of the ionosphere. Computed density profiles for $N(^4S)$, $N(^2D)$, $N(^2P)$, and NO are presented. We found that the model NO densities are about a factor of 2–3 less than those measured by the Viking 1 mass spectrometer. The computed and measured values can be brought into agreement if the rate coefficient for reaction of N with NO (reaction (R19)) is assumed to be smaller at the low temperatures of the Martian thermosphere, which are below the temperature range of validity of the currently recommended value [DeMore et al., 1992]. A small activation energy for the reaction and thus smaller values of the rate coefficient at the temperatures in the lower Martian thermosphere are indicated by the measurements of Clyne and McDermid [1975] and Davidson and Hanson [1990].

We have also computed revised values for the escape rates of N atoms from dissociative recombination and ionospheric reactions. We find that dissociative recombination is comparable in importance to photodissociation at low solar activity, but it is still the most important escape mechanism

for ^{14}N at high solar activity. For our standard model we compute a current ^{14}N escape rate averaged over high and low solar activity of $4.8 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Integrating backward in time, we find that if the escape is uninhibited, the predicted $^{15}N/^{14}N$ ratio would be a factor of 4 times the terrestrial value, and the initial column density of N_2 would be $7.8 \times 10^{22} \text{ cm}^{-2}$, about 13 times the current abundance. If a dense early CO_2 atmosphere of 1–2 bars existed that was lost exponentially with a time constant of $2.2 - 2.6 \times 10^{16} \text{ s}$ ($\sim 700\text{--}800 \text{ m.y.}$), the measured isotope ratio is obtained.

The predicted $^{15}N/^{14}N$ isotope ratio and initial column density of N_2 are, however, highly dependent on assumptions made about the dissociative recombination of N_2^+ at the exobase in the Martian ionosphere: on the rate coefficient, electron temperatures and yield of the $N(^2D) + N(^4S)$ channel. Although much of the previous uncertainty about the electron temperatures has been resolved, there is still controversy about the rate coefficient for dissociative recombination from the ground state of N_2^+ , little information about that from excited states, and almost a factor of 10 discrepancy between measurements and calculations for the yield of channel (R1a). Modest variations about our standard values change the initial CO_2 pressure required (or, equivalently) the time constant for loss of a dense early atmosphere but have little effect on the basic conclusion, that such an atmosphere is required to suppress the escape of N atoms early in the planet's history.

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