The Regulation of Hydrogen and Oxygen Escape from Mars

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It is shown that under present conditions the Jeans escape flux of hydrogen from Mars in the form of H and H_2 is constrained to be the same as twice the non-thermal (McElroy, 1972) escape of O atoms. The mediation of the chemical chain that recombines CO_2 plays an essential role in regulating the escape of hydrogen to match that of oxygen, confirming a mechanism postulated by McElroy and Donahue (1972). It is also shown that if the oxygen flux changes, a change in the O_2 mixing ratio results and the consequence is to induce a large change in the odd hydrogen concentration, and consequently in H_2 production and hydrogen escape. The effect is to stabilize the hydrogen escape flux at twice the O flux. It is shown that surface chemistry should not change the operation of this mechanism but has consequences for the eddy coefficient variation at low altitudes. There is a strong correlation between low humidity, large solar zenith angles and large O_3 abundances. The effect of argon in a mixing ratio as large as 0.3 on these results is also investigated.
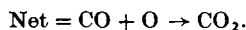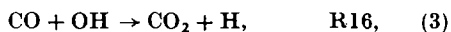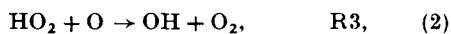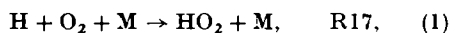
I. INTRODUCTION

One of the fundamental problems of atmospheric chemistry is that of understanding the stability of CO_2 in the atmospheres of Mars and Venus. There are problems in understanding the low degree of dissociation in the low as well as in the upper atmospheres of each planet. They stem from the fact that, whereas CO_2 undergoes photolysis at a global mean rate of $3 \times 10^{12} cm^{-2} sec^{-1}$ (in the atmosphere of Mars) and only very slowly recombines from CO and O (^3P), the concentrations of CO and atomic oxygen are very low in the upper atmosphere and the mixing ratios of CO and O_2 are also low for the atmosphere as a whole, attaining a value of only about $10^{-3} v/v$. Yet the three-body rate constant for recombination of O with CO is very small, $2 \times 10^{-37} cm^6 sec^{-1}$, compared to that for formation of O_2 from two oxygen atoms under equivalent conditions, $7 \times 10^{-33} cm^6 sec^{-1}$. The amount of atomic oxygen in the upper atmosphere can be created by photolysis of CO_2 in about $1.5 \times 10^3 sec$. It has been shown that there is only one viable solution to the problem of maintaining the ratio of atomic oxygen to CO_2 near 135km at a value between 5×10^{-3} and 10^{-2} (Strickland et al., 1972). It is necessary to remove the oxygen at an effective downward velocity of 500 to 100cm/sec (Donahue, 1971; McElroy and McConnell, 1971). This is equivalent to an eddy diffusion coefficient between 5 and $10 \times 10^8 cm^2 sec^{-1}$ above 100km if the transport is considered to occur because of eddy diffusion.

But in the lower atmosphere O_2 apparently should form in great amounts even if the oxygen is rapidly removed from the upper atmosphere. The observed amount is 1.3×10^{-3} times the CO_2 abundance (Barker, 1972; Carleton and Traub, 1972) and the photolysis rate is $5 \times 10^{10} cm^{-2} sec^{-1}$. This gives every O_2 molecule a very long lifetime, about $10^{10} sec$ against this form of destruction. In view of the large three-body formation rate it is necessary to find a way, other than photolysis, to break O_2 bonds at a rapid rate, to keep the production rate of O_2 to a very low value, or to find a mechanism that combines some measure of both of these properties.

The literature already contains excellent

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reviews of some of the material in this introduction (McConnell, 1973; Hunten, 1974; McElroy, 1974). Since this paper is a contribution to a symposium, it will repeat parts of these reviews. A model that depends predominantly on the solution involving breaking the O_2 bonds was proposed by Parkinson and Hunten (1972), and it is discussed later in this paper. A solution that essentially short-circuits O_2 formation was favored in a model proposed by McElroy and Donahue (1972). This second solution features a scheme for recombination of O and CO rather than O and O and involves bringing atmic oxygen down to the neighborhood of 30km so rapidly that it has almost no chance of recombining by forming O_2 before the radical HO_2 begins to be produced in a three-body reaction at a rapid rate. This enables a catalytic cycle to operate efficiently:

$$H + O_2 + M \rightarrow HO_2 + M, \quad R17, \quad (1)$$

$$HO_2 + O \rightarrow OH + O_2, \quad R3, \quad (2)$$

$$CO + OH \rightarrow CO_2 + H, \quad R16, \quad (3)$$

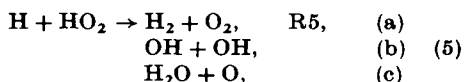$$\text{Net} = CO + O \rightarrow CO_2.$$

The hydrogen atoms are supplied by dissociation of H_2O. The eddy diffusion coefficient required to produce such effective transport has to be greater than 1.5×10^8 cm^2sec^{-1} at all altitudes above 30km.

Almost all of the O_2 in the system is formed by the reaction

$$O + OH \rightarrow O_2 + H, \quad R2, \quad (4)$$
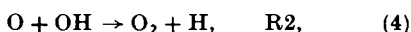
between 25 and 30km. Photolysis of O_2 in the Herzberg continuum, occurring mostly between 2 and 15km, is the major sink for O_2 although some destruction results from photolysis of H_2O_2 after its formation from HO_2 below 10km. Several conditions are imposed on the system. The principal one is that the integrated rates of reactions (1) to (3) be equal to the integrated rate of production of O atoms by photolysis of CO_2 and to each other. Subsidiary conditions are that the production of H_2 from branch (a) of the reaction

$$
\begin{aligned}
H + HO_2 &\rightarrow H_2 + O_2, \quad R5, \quad \text{(a)} \\
&\quad OH + OH, \quad\quad\quad \text{(b)} \quad (5) \\
&\quad H_2O + O, \quad\quad\quad \text{(c)}
\end{aligned}
$$

be half the thermal (Jeans) escape flux of H atoms and that the formation of H_2O from the reaction

$$OH + HO_2 \rightarrow H_2O + O_2, \quad R7, \quad (6)$$
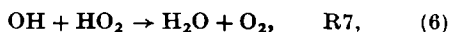
equal the rate of photolysis of $15\mu m$ of precipitable water (5×10^{19} molecules cm^{-2}) (Schorn, 1971; Barker et al., 1970; Conrath et al., 1973). This is to say that water is made at a rate of about 2×10^9 molecules $cm^{-2}sec^{-1}$. The O_3 abundance is $1.4\mu m$-atm in the model and this is well below the limit of $3\mu m$-atm set by uv spectroscopy (Barth et al., 1973; Barth and Dick, 1974) in regions where the amount of water vapor lies in the range $10-20\mu m$ of precipitable water. The ozone in this model is also concentrated close to the surface. Since it is the odd hydrogen resulting from water vapor dissociation that suppresses the odd oxygen in this model, it is not qualitatively surprising that as much as 10 to $60\mu m$-atm of O_3 were detected by Mariner 9 (Barth and Dick, 1974) above the polar caps where there is less than $1\mu m$ of precipitable water.

The photochemical scheme proposed seems to offer a natural explanation for the discovery by McElroy (1972) that atomic oxygen escapes from Mars at the rate of about 7×10^7 atoms $cm^{-2}sec^{-1}$, or about half the thermal escape rate of hydrogen and consequently that there is no accumulation of oxygen on the planet. An H escape flux of $1.8 \times 10^8 cm^{-2}sec^{-1}$ would leave behind 2.4×10^{20} molecules cm^{-2} in 10^5yr. This is the amount now found in the atmosphere. Thus there is another problem of accounting for the lack of oxygen on the planet, that of disposing of the O_2 belonging to the H_2O which has lost its hydrogen. McElroy's nonthermal escape mechanism for atomic oxygen is based on the recognition that dissociative recombination of CO_2^+ and O_2^+ with electrons produces oxygen atoms in both cases, whether the products of dissociation are electronically excited or not, with greater than their escape energy of $1.99eV$. Hence about half the ions created above the exobase will produce oxygen atoms traveling upward with greater than escape velocity. McElroy and Donahue (1972) argued that the balance

between the hydrogen escape flux and the oxygen escape flux was probably not an accident. They reasoned that in their chemical scheme the rate of oxygen escape determined the rate of hydrogen escape by determining the magnitude of the integral

$$I_1 = \int k_5[H][HO_2]\,dz, \qquad (7)$$

where the bracket denotes as usual the density of the species enclosed. This integral gives the rate at which H_2 molecules are formed. These then flow upward to supply the escaping hydrogen atoms. A decrease in atomic oxygen escape flux would lead to an increase in CO and O_2 concentration and hence a decrease in odd hydrogen. This follows because the integrals

$$I_2 = \int k_{16}[CO][OH]\,dz$$
$$= \int k_{17}[H][O_2][M]\,dz \qquad (8)$$

and

$$I_3 = \int k_7[OH][HO_2]\,dz \qquad (9)$$

that determine the rate of CO_2 and H_2O recombination are constrained to remain invariant.

However, in the calculations of McElroy and Donahue (1972) it was not verified that the detailed solution of the coupled flow equations from the surface to the base of the exosphere produced the observed escape flux of hydrogen. Nor was it demonstrated that changing the oxygen escape flux would indeed provoke a change in hydrogen escape in such a way as to drive the system to a new stable state in which oxygen and twice hydrogen escape fluxes would again be equal. That thesis is not self-evident, particularly in view of the recent work of Hunten (1973), Hunten and Strobel (1974), and Liu and Donahue (1974a, 1974b, 1974c) showing that the escape flux of hydrogen on Earth is determined by the mixing ratio of hydrogen compounds in the stratosphere and very little influenced by factors such as the rates of transport, chemical or dissociative processes in the mesosphere and lower thermosphere. This is the case when the temperature is sufficiently high in the exosphere to establish limiting flux conditions. Thus one might expect the mixing ratio of water

in the stratosphere to control the escape rate of hydrogen on Mars since the mixing ratio of H_2O is assumed to remain constant. However, it will appear in the course of this paper that limiting flux in fact does not occur on Mars, that the oxygen flux is in fact equal to half the hydrogen flux as calculated in the model under present Martian conditions, and that the oxygen flux does indeed control the hydrogen flux. The validity of the last statement will be demonstrated by assuming that, while the atmosphere remains unchanged in its CO_2 and H_2O contents and in the vertical profiles of temperature and eddy coefficient, the O_2 abundance is different from its present value. It will be shown that under such circumstances the quasi-steady state calls for a change in H and H_2 densities at the base of exosphere considerably greater in magnitude and opposite in sense to the change in the amount of O_2 in the atmosphere. Then the effective escape rate of H_2 and O would be unbalanced. This would not represent a true steady state, however, because H_2 and thus the escaping hydrogen is produced by branch (a) of R5 involving O_2. Thus, for example, suppose that the nonthermal escape flux of atomic oxygen for some reason, such as enhanced solar euv flux were to double. The O_2 mixing ratio would then begin to decrease, approaching a value half the present one. But the hydrogen escape flux would increase even faster and attain a value equal to twice the O flux before O_2 could reach half its present concentration. The escape of water would then be stabilized at a new value. The hydrogen escape flux could not continue to increase because, since its source is R5a, it must be in balance with the production of HO_2. Enhanced production of HO_2 would not be possible if the O_2 concentration were to continue to decrease. Thus the new steady state would be one in which the escape of water is double the present rate, but the O_2 concentration more than half its present value.

II. HYDROGEN ESCAPE FLUX

Our technique is the one described in our papers on hydrogen chemistry and

escape for Earth and Venus (Liu and Donahue, 1974a, 1974b, 1974c, 1975). A standard CO_2 model atmosphere with an exosopheric temperature of 320K is assumed (NASA, 1974). The O_2 and precipitable H_2O abundances are fixed at 1.3×10^{-3} [CO_2] and 15μm. The density of

atomic hydrogen at the exobase, 226km, is fixed at 3×10^4cm^{-3} (Anderson, 1973) so that the thermal escape flux of atomic hydrogen is predetermined. Coupled diffusion equations involving eddy and Fickian diffusion are solved for the densities of CO, O_2, H_2, H_2O, H_2O_2, HO_x, and

TABLE I

Reaction number	Reaction	Rate constant	Reference
R1	$H + O_3 \rightarrow OH + O_2$	$k_1 = 2.6 \times 10^{-11}$	a
R2	$OH + O \rightarrow H + O_2$	$k_2 = 5 \times 10^{-11}$	b
R3	$HO_2 + O \rightarrow OH + O_2$	$k_3 = 5 \times 10^{-11}$	c,d
R4	$H + HO_2 \rightarrow OH + OH$	$k_4 = 10^{-10}\exp(-330/T)$	e
R5	$H + HO_2 \rightarrow H_2 + O_2$	$k_5 = 3 \times 10^{-11}\exp(-330/T)$	e
R6	$OH + OH \rightarrow H_2O + O$	$k_6 = 2 \times 10^{-12}$	c
R7	$OH + HO_2 \rightarrow H_2O + O_2$	$k_7 = 2 \times 10^{-10}$	d
R8	$OH + H_2 \rightarrow H_2O + H$	$k_8 = 3.8 \times 10^{-11}\exp(-2600/T)$	g
R9	$O + H_2 \rightarrow OH + H$	$k_9 = 7 \times 10^{-11}\exp(-5000/T)$	c
R10	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{10} = 3 \times 10^{-11}\exp(-500/T)$	h
R11	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$k_{11} = 4.1 \times 10^{-11} T^{1/2}\exp(-600/T)$	i
R12a	$H_2O_2 + O \rightarrow H_2O + O_2$	$k_{12a} = 2.3 \times 10^{-11}\exp(-3200/T)$	j
R12b	$H_2O_2 + O \rightarrow OH + HO_2$	$k_{12b} = 2.3 \times 10^{-11}\exp(-3200/T)$	j
R13	$O(^1D) + H_2O \rightarrow 2OH$	$k_{13} = 3 \times 10^{-10}$	k
R14	$O(^1D) + H_2 \rightarrow OH + H$	$k_{14} = 3 \times 10^{-10}$	k
R15	$O(^1D) + CO_2 \rightarrow O + CO_2$	$k_{15} = 1.8 \times 10^{-10}$	l
R16	$CO + OH \rightarrow H + CO_2$	$k_{16} = 9 \times 10^{-13}\exp(-500/T)$	c
R17	$H + O_2 + CO_2 \rightarrow HO_2 + CO_2$	$k_{17} = 2 \times 10^{-13} (T/273)^{-1.3}$	n
R18	$CO + O + CO_2 \rightarrow CO_2 + CO_2$	$k_{18} = 2 \times 10^{-37}$	o,p,q
R19	$O + O + CO_2 \rightarrow O_2 + CO_2$	$k_{19} = 3 \times 10^{-33} (T/300)^{-2.9}$	c
R20	$O + O_2 + CO_2 \rightarrow O_3 + CO_2$	$k_{20} = 1.4 \times 10^{-33} (T/300)^{-2.5}$	c
R21	$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$	$k_{21} = 1.4 \times 10^{-9}$	r
R22	$CO_2H^+ + e \rightarrow CO_2 + H$	$k_{22} = 3.5 \times 10^{-7}$	Assumed
R23	$O^+ + CO_2 \rightarrow O_2^+ + CO$	$k_{23} = 1.2 \times 10^{-9}$	r
R24	$O^+ + H_2 \rightarrow OH^+ + H$	$k_{24} = 2.0 \times 10^{-9}$	r
R25	$H^+ + O \rightarrow O^+ + H$	$k_{25} = 3.8 \times 10^{-10}$	s
R26	$O^+ + H \rightarrow H^+ + O$	$k_{26} = 6.8 \times 10^{-10}$	s
R27	$O_2^+ + e \rightarrow O + O$	$k_{27} = 8.75 \times 10^{-6} (Te)^{-0.67}$	t
R28	$CO_2^+ + e \rightarrow CO + O$	$k_{28} = 1.14 \times 10^{-4} (Te)^{-1}$	u
R29	$OH^+ + e \rightarrow H + O$	$k_{29} = 2.2 \times 10^{-7}$	Assumed
R30	$CO_2^+ + O \rightarrow O_2^+ + CO$	$k_{30} = 1.6 \times 10^{-10}$	v
R31	$CO_2^+ + O \rightarrow O^+ + CO_2$	$k_{31} = 9.6 \times 10^{-11}$	v

a Phillips and Schiff (1962).
b Clyne and Thrush (1963a).
c Kaufman (1964, 1969a, 1969b).
d Hochanadel et al. (1972).
e Schofield (1967).
g Wilson (1972).
h Hampson et al. (1973).
i Greiner (1968).
j Albers et al. (1971).
k Biedenkapp et al. (1970).

i Clark and Noxon (1972).
n Baulch et al. (1969).
o Simonaitis and Heicklen (1972).
p Stuhl and Niki (1971).
q Slanger et al. (1972).
r Fehsenfeld et al. (1969).
s Fehsenfeld and Ferguson (1972).
t Walls and Dunn (1974).
u Bauer (1973).
v Fehsenfeld et al. (1970).

O_x from the surface of Mars to its exobase. Odd hydrogen HO_x comprises the rapidly interconverting species H, OH and HO_2 while O_x comprises O, O_3, OH and HO_2. Every species is required to satisfy the standard diffusion equation, the continuity equation, and

$$\int_0^{226\,km} [p_i(z) - l_i(z)]dz = \phi_i(226\,km) - \phi_i(0\,km), \quad (10)$$

where ϕ_i, p_i, and l_i are local flux, production rates and loss rates for the ith atmospheric species. Except for H_2O we assume no flux at the surface. The H_2O outgassing rate is taken to be equal to one-half the hydrogen escape flux. It is also required that the mixing ratio of CO in an acceptable solution fall within the observed range 7×10^{-4} to 3.2×10^{-3} (Carleton and Traub, 1972; Young, 1971). The mixing ratio of CO is otherwise allowed to vary, as is the eddy diffusion coefficient, until we obtain a solution satisfying the constraints. In arriving at our model we calculate ion density profiles, varying the solar ionizing flux to obtain agreement with Mariner 9 election density profiles. The ionospheric model is important, of course, in determining the rate of oxygen escape and the rate of conversion of H_2 to H. In Table I we present the chemical, ion-molecule, ion-electron and photolysis rate constants used in our model calculations.

It is immediately apparent that assuming the water vapor concentration to be determined by mixing and photochemical processes alone from the surface upward produces serious problems. The difficulty is that when there is sufficient H_2O to supply by photolysis the hydrogen atoms that rise to the exobase, photolysis occurs in the
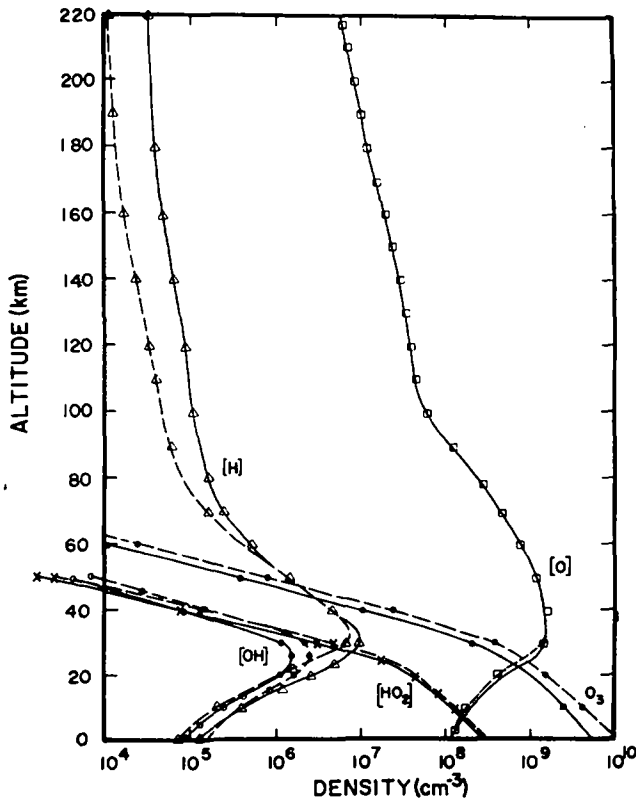

FIG. 1. Density distributions of H, OH, HO_2, O, and O_3 for two values of the O_2 mixing ratio: 1.3×10^{-3} and 2.6×10^{-3}. Solid lines correspond to 1.3×10^{-3} O_2 mixing ratio and dashed lines correspond to 2.6×10^{-3} O_2 mixing ratio.

neighborhood of 30 to 40km and the OH density is so high that the production of O_2 by the reaction R2(4) is prohibitively large. Therefore, it is necessary to assume instead (a reasonable assumption after all) that H_2O follows a saturation profile from the surface to 15km (Hunten and McElroy, 1970). The scale height of this distribution is so small that virtually all the precipitable H_2O is contained below 10km. The H_2O density at the surface is $6 \times 10^{14} cm^{-3}$, while that at 10km is fixed at $2 \times 10^9 cm^{-3}$. Above 15km the H_2O is assumed to obey the coupled flow equations. The great advantage of this assumption is the H_2O supplies the odd hydrogen precisely where it is needed for the recombination cycle (near the surface) by reaction R13 of H_2O with $O(^1D)$, where the latter species is produced in turn from O_3 photolysis. The odd hydrogen also provides a large source of H_2 at low altitudes (near 25km) through the reaction branch (5a).

If we assume that the rate constant for this branch of the H, HO_2 reaction is $3 \times 10^{-11}exp(-330/T)$, as McElroy and Donahue (1972) did, then the H_2 is virtually the sole source of escaping hydrogen atoms, and it supplies them in the ionospheric reactions

$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H, \qquad R21, \quad (11)$$

$$CO_2H^+ + e \rightarrow H + CO. \qquad R22. \quad (12)$$
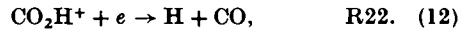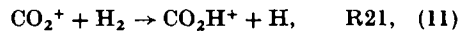
The density of H_2 at the exobase is $1.3 \times 10^5 cm^{-3}$, larger than that of H by a factor of about 4. However, the effusion velocity of H_2 is so much lower than that of H that twice the escape flux of H_2 is only 24% the escape flux of H. $2\phi_{H_2}$ is 2.1×10^7 $cm^{-2}sec^{-1}$ while $\phi_H \times 8.7 \times 10^7 cm^{-2}sec^{-1}$ and the total hydrogen flux is 1.1×10^8 $cm^{-2}sec^{-1}$. Near 100km the mixing ratio of H_2 in this scheme is 16ppm. To account for the L_α airglow observed by Mariners 6, 7, and 9, Anderson (1973) was obliged to assume a source for atomic hydrogen
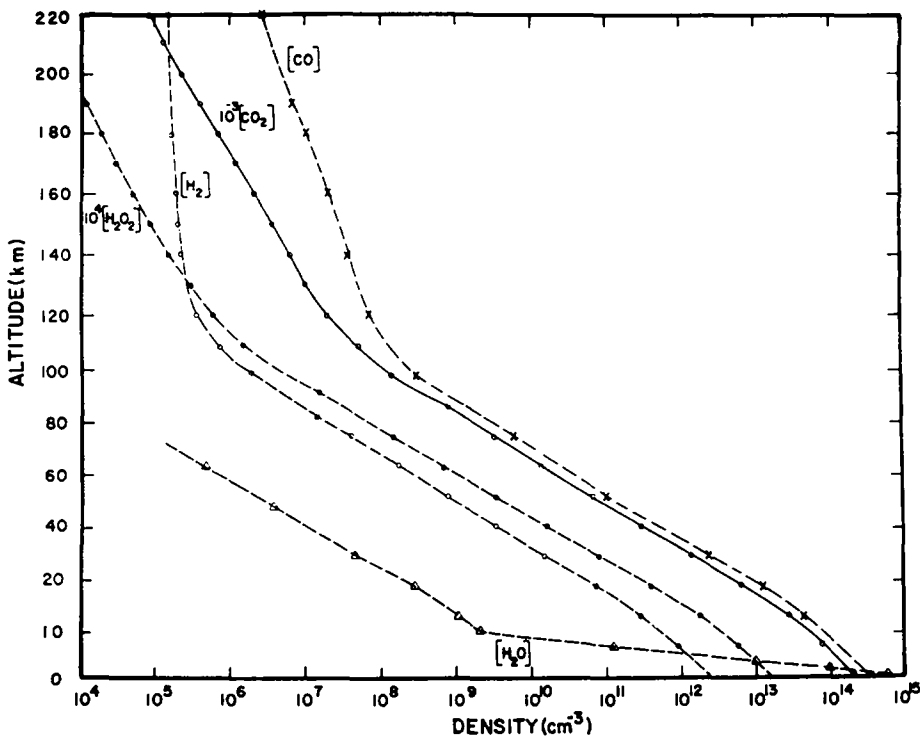

FIG. 2. Density distributions of H_2, H_2O, H_2O_2, and CO for $1.3 \times 10^{-3} O_2$ mixing ratio. Profiles corresponding to $2.6 \times 10^{-3} O_2$ mixing ratio can be obtained by shifting these curves linearly according to the ratio listed in Table II.

which required 20ppm of H_2 in the mesosphere and lower thermosphere. Thus, support is lent to this model by the L_α observations.

In Figs. 1 and 2 we show the densities of important species between the surface and 226km under two assumptions concerning the values of the O_2 mixing ratio: 1.3×10^{-3} and 2.6×10^{-3}. In the "normal" case the surface volume mixing ratios are $[CO]_0 = 1.55 \times 10^{-3}$, $[O_2]_0 = 1.3 \times 10^{-3}$, $[H_2O_2]_0 = 7 \times 10^{-9}$, $[H_2]_0 = 11 \times 10^{-6}$ and $\int [H_2O]dz = 5 \times 10^{19} cm^{-2}$ (15μm of precipitable water). The abundance of ozone is $5.8 \times 10^{15} cm^{-2}$ or 2.15μm-atm. The distribution of odd hydrogen and odd oxygen very closely follows that shown by McElroy and Donahue (1972, Fig. 1). In the ionosphere it is necessary to assume euv fluxes 2.7 times as large as the Hinteregger (1970) values to obtain electron and ion densities that agree with Mariner observations.

The fluxes of hydrogen and oxygen species in the "normal" case are plotted in

Figs. 3 and 4. There are several interesting features to notice in these flux curves. The escape flux of O is supplied below the exobase by an upward flow of CO_2 since CO_2 is the species that is ionized in the exosphere. The return flux of CO from the exosphere is exactly the CO_2 at the exobase. The downward flux of atomic oxygen at the exobase is only half the return flux of CO because half the oxygen resulting from dissociative recombination of CO_2^+ and O_2^+ escapes while none of the CO does. Oxygen and CO flow downward, after being produced by dissociative recombination in the ionosphere. The rate of flow is enhanced below 90km because of CO_2 photolysis. Near 30km both begin to be destroyed through reactions R2, R10, and R16. Molecular oxygen is made just above 30km by reaction R2 and dissociated in the Harzberg continuum below 15km and by HO_2 association. H_2O is produced near 33km as a result of the reaction of the odd hydrogen radicals OH and HO_2 (R7). It is
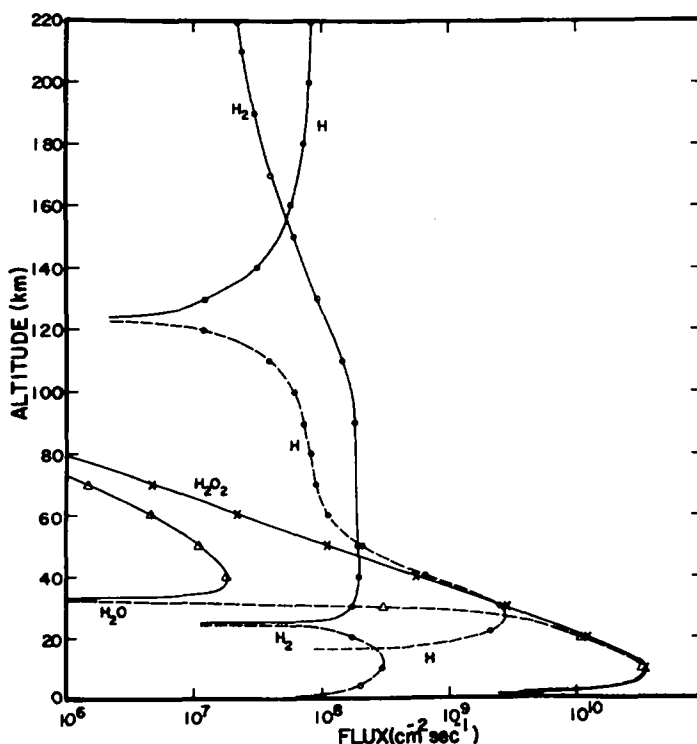

FIG. 3. Fluxes of odd hydrogen (indicated by H) H_2, H_2O, and H_2O_2 for $1.3 \times 10^{-3} O_2$ mixing ratio. Solid lines indicate upward fluxes and dashed lines indicate downward fluxes.
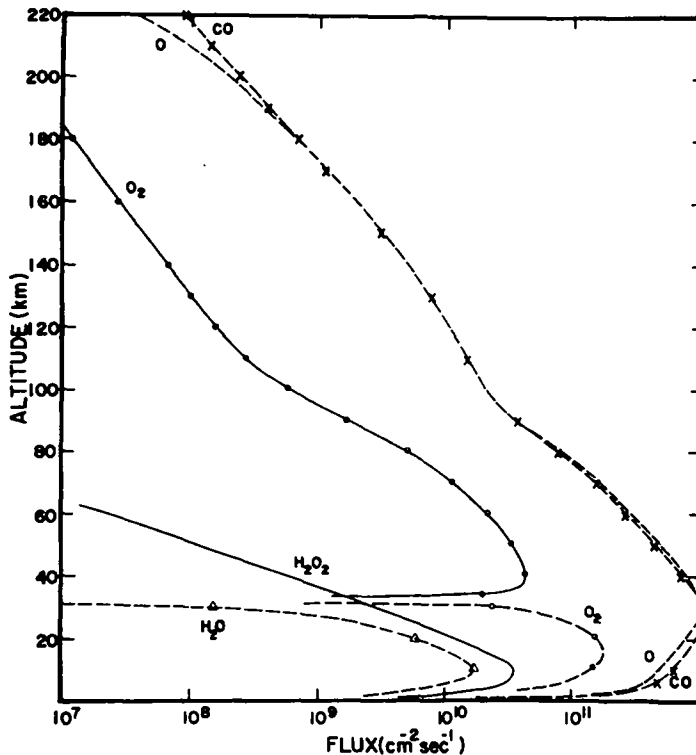
FIG. 4. Fluxes of odd oxygen (indicated by O) CO, O_2, H_2O_2, and H_2O corresponding to the same condition of Fig. 3. Solid lines and dashed lines indicate upward and downward fluxes, respectively.

photolyzed above 40km and dissociated by $O(^1D)$ (produced from O_3) below 8km, where it is by far the dominant source of odd hydrogen. It is interesting that the downward flux of H_2O below about 25km and the upward flux of H_2O_2 formed by reacting pairs of HO_2 are almost numerically equal. The flux, $-\phi(H_2O)$, is about $1.7 \times 10^{10} cm^{-2}sec^{-1}$ at 10km while $\phi(H_2O_2)$ is $1.74 \times 10^{10} cm^{-2}sec^{-1}$. H_2 is clearly produced at about 25km by the reaction of H and HO_2 (R5). It flows downward to be dissociated by $O(^1D)$ below 12km, thereby recycling odd hydrogen in the chemosphere. But the upward flux begins to run into CO_2^+ in significantly large amounts near 100km. The reactions R21 and R22 make hydrogen atoms near 123km. Some of these atoms flow upward in ever increasing numbers until at the exobase they supply an escape flux of $8.7 \times 10^7 H$ atoms $cm^{-2}sec^{-1}$. However, there is a very sizable supply of H_2 still
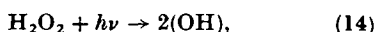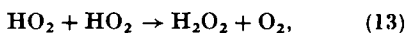
remaining at the exobase and it supports an escape flux of H_2 that amounts to 2.1×10^7 atoms $cm^{-2}sec^{-1}$. The sum is very close to twice the oxygen escape flux of $1.07 \times 10^8 cm^{-2}sec^{-1}$.

It is necessary to use a large value for the eddy diffusion coefficient in the upper atmosphere as well as in the lower atmosphere to make this scheme work: 4×10^8 cm^2sec^{-1} in fact. Not only is this strong mixing required to bring oxygen atoms down to 30km rapidly enough to reach the region where they can form HO_2 in a three-body reaction before they form O_2 in forbiddingly large quantities, but large values of K are also needed to transport downward rapidly enough the H formed from the reaction of H_2 and CO_2^+ and prevent [H] at the exobase from growing greater than the value $3 \times 10^4 cm^{-3}$.
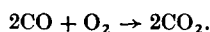
It is very important to notice that because of the relatively low density of CO_2^+, such a large fraction of H_2 remains undis-

sociated at the exobase that the limiting flux condition of Hunten (1973) is not achieved. The exospheric temperature is so low that, because of the large fraction of hydrogen in the form of H_2 at high altitudes, the bottleneck for escape is at exobase. There is a large upward flux of H_2 to the ionosphere and a large downward flow of H to form H_2 and HO_2 in the lower atmosphere. The escape flux is thus not controlled by the supply of hydrogen in the stratosphere and the mechanism involving control of H (and H_2) escape by the nonthermal atomic oxygen escape rate can operate.

The value of the rate constant R5a for H_2 production in the H, HO_2 reaction is $3 \times 10^{-11} \exp(-330/T) cm^3 sec^{-1}$. This is the value favored in the CIAP tables (Garvin and Hampson, 1974). It is also very important in selecting between this recombination scheme and that of Parkinson and Hunten (1972). This latter scheme is essentially a photochemical one in which the O_2 bond is broken after a step of peroxide formation and photolysis added to reactions (1) and (3)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \qquad (13)$$

$$H_2O_2 + h\nu \rightarrow 2(OH), \qquad (14)$$

amounting to

$$2CO + O_2 \rightarrow 2CO_2.$$

The supply of odd hydrogen needs to be much higher in this model than in that of McElroy and Donahue (1972). Unless the rate constant k_5 (a) is no larger than about $3 \times 10^{-12} cm^3 sec^{-1}$, there is more H_2 formed than may be destroyed by $O(^1D)$ and the ion molecule reactions (11) and (12).

III. RELATIONSHIP AMONG O_2 ABUNDANCE, O AND H ESCAPE RATES

We have also performed the exercise of allowing the O_2 mixing ratio to increase from 1.3×10^{-3} in stages to 2.6×10^{-3}. In performing this exercise we keep the CO_2 and H_2O content of the atmosphere fixed, as well as the eddy diffusion coefficient. Thus the integrated rates of CO and O

production and recombination along with H_2O dissociation and reformation rates must remain unchanged. We find that if we arbitrarily increase the O_2 content of the atmosphere to a new value the H density and H_2 density at the exobase decrease. The factor by which the escape fluxes decrease is, however, always greater than the factor by which the O_2 content of the atmosphere is assumed to increase. Thus if we change the mixing ratio of O_2 from 1.3×10^{-3} to 2.6×10^{-3}, the H density at the exobase goes from 3.1×10^4 to $1.1 \times 10^4 cm^{-3}$, and the H_2 density from 1.4×10^5 to $5.0 \times 10^4 cm^{-3}$ (Note that H_2 and H decrease by the same factor.) The escape fluxes go to the values

$$\phi(H) + 2\phi(H_2) = 3 \times 10^7 + 7.7 \times 10^6 \quad (15)$$

or $3.8 \times 10^7 cm^{-2} sec^{-1}$ in place of 1.1×10^8 $cm^{-2} sec^{-1}$.

In Fig. 5 we show the hydrogen fluxes for the case of doubled O_2 abundance. The chain that begins with an increase in O_2 mixing ratio and ends in a decrease in the hydrogen density at the exobase is the following. The ozone abundance grows along with the O_2 abundance because of reaction R20. The result is a doubling in $[O_3]$ and a doubling of the rate of production of $O(^1D)$. The lifetime of H_2 against destruction by $O(^1D)$ thus is cut in two. Meanwhile the reaction of H with O_2 (R17) causes [H] to decrease and $[HO]_2$ together with [OH] to increase. The effect is to cause a decrease in total H_2 production in the reaction between H and HO_2 (R5). The combined effect of enhanced destruction and diminished production causes the overall decrease in the H_2 density, and consequently the decrease in both H_2 and H density at the exobase, since H is derived from H_2 in the upper atmosphere via the ionosphere reactions R21 and R22.

An increase in the O_2 mixing ratio by 50% to 1.95×10^{-3} provokes a decrease in H and H_2 densities at the exobase by a factor of 1.8 with a corresponding decrease in escape flux. It will be noted that in Figs. 1 and 2 there are only small changes in most atmospheric constituents apart from H, H_2, and CO in response to these large changes in O_2. These changes are
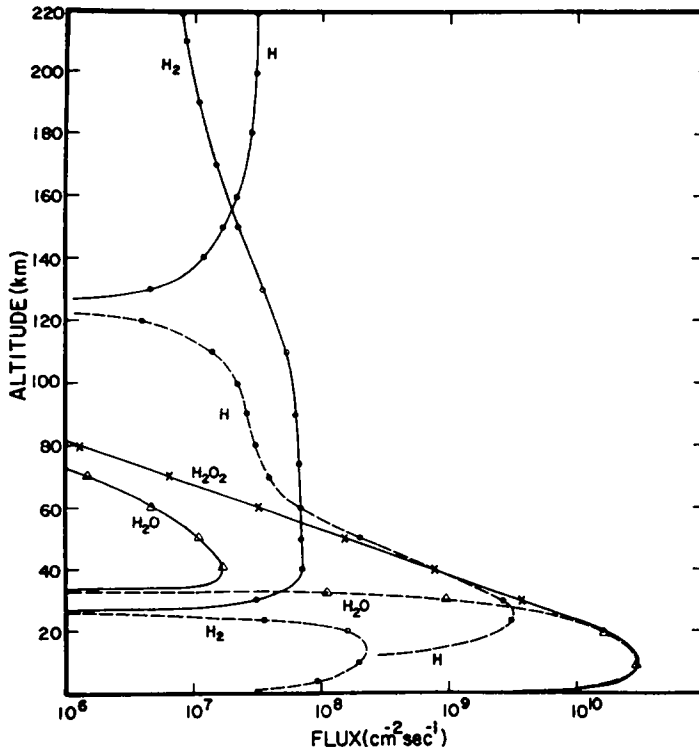
FIG. 5. Fluxes of odd hydrogen (indicated by H) H_2, H_2O, and H_2O_2 for $2.6 \times 10^{-3} O_2$ mixing ratio. Solid lines indicate upward fluxes and dashed lines indicate downward fluxes.

TABLE II

RESPONSE OF ATMOSPHERIC CONSTITUENTS TO CHANGES IN O_2 MIXING RATIO

$[O_2]_0$	$1.3 \times 10^{-3} [CO_2]$	$1.95 \times 10^{-3} [CO_2]$	$2.6 \times 10^{-3} [CO_2]$
$[CO]_0$	$1.6 \times 10^{-3} [CO_2]$	$1.27 \times 10^{-3} [CO_2]$	$1.03 \times 10^{-3} [CO_2]$
$[H_2]_0$	$1.1 \times 10^{-5} [CO_2]$	$6.1 \times 10^{-6} [CO_2]$	$3.9 \times 10^{-6} [CO_2]$
$[H_2]_{226}$	$1.4 \times 10^5 cm^{-3}$	$7.9 \times 10^4 cm^{-3}$	5.0×10^4
$[H]_{226}$	$3.1 \times 10^4 cm^{-3}$	1.77×10^4	1.1×10^4

summarized in Table II. Naturally the CO mixing ratio must decrease as the O_2 mixing ratio increases, because there are relatively more HO_2 and OH than H atoms due to reaction (R17), and the CO mixing ratio must decrease to keep (I_2) constant.

Now it must be realized that we have not performed a time-dependent calculation in which the O escape flux was caused to vary by some mechanism—change in exobase level, or change in euv flux, for example—and the development of the O_2 mixing ratio tracked along with the

hydrogen escape flux as the oxygen flux varied. This would demonstrate that twice the hydrogen escape rate accurately follows the oxygen escape rate if the change is slow, or tends to that rate following a sudden change. To do so would require more computer facilities than we have. Furthermore, it is not necessary, for we have shown that changing the O_2 mixing ratio has a profound effect on the H escape flux, since the escape flux changes by a larger factor than the change of the total O_2 content of the atmosphere. Therefore,

it may be argued that if in reality the non-thermal atomic oxygen escape rate were to change, whether slowly or suddenly, the effect would be necessarily to cause the O_2 content of the atmosphere to change in the opposite sense, and this, as we have seen, would provoke a change in the hydrogen escape flux in the same sense as the change in the O flux. Furthermore, small changes in O_2 provoke large changes in H_2 concentration, and consequently in H production, because of the role played by HO_2. It follows necessarily, therefore, that the hydrogen escape flux will change in response to the change in oxygen flux. As soon as that flux reaches a new steady-state value, the atmosphere will settle down to a new steady state in which half the hydrogen flux is equal to the oxygen flux and the O_2 content of the atmosphere has a new equilibrium value. Of course we can conclude from the exercise we have conducted that the O_2 reduction provoked by a factor of 2 increase in the O escape rate will be by less than a factor of 2. There is however, no possibility that an increase, say, in the oxygen escape rate, will cause a runaway in which the decrease in O_2 in the atmosphere provokes a larger response in hydrogen flux than the oxygen

escape flux that caused the O_2 to decrease. The reason is that an overshoot in the hydrogen escape will cause the O_2 in the atmosphere to begin to build up again and to cause the H escape rate to diminish. Thus the system is a stable one.

IV. O_3, H_2O, AND THE POLAR CAP

It is important to investigate the condition of the atmosphere above the winter and spring polar cap. It has been observed that the water vapor content of the atmosphere drops below the minimum detectable value of $10\mu m$ (less than $0.5\mu m$ according to results reported from Mars 3), while ozone is observed to rise to as much as 10 to $15\mu m$-atm just after sunrise over the polar cap. We would expect a decrease in water vapor to provoke a reduction in odd hydrogen in the lower atmosphere and thus to cause an increase in the O_3 abundance. To test the quantitative nature of this effect, we have let the water vapor content of the atmosphere decrease in steps from $15\mu m$ to 7.5, 3.7, 0.3 down to $3 \times 10^{-3}\mu m$. The atmosphere is otherwise assumed to be identical with the standard one we developed at lower latitudes, i.e., to have the same eddy coefficient profile,
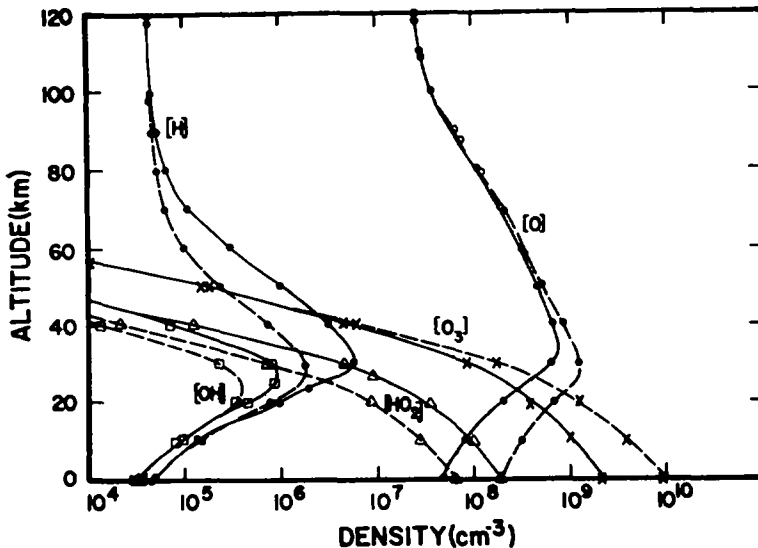

FIG. 6. Density distributions of H, OH, HO_2, O, and O_3 for winter polar region. Solid lines correspond to $15\mu m$ of H_2O and dashed lines correspond to $0.3\mu m$ of H_2O.

TABLE III

H_2O COMPARED TO O_3 CONCENTRATION
OVER THE SPRING POLAR CAP

H_2O (μm)	O_3 (μm-atm)
15	0.92
7.5	1.4
3.7	2.0
0.3	3.9
3×10^{-3}	5.2

and, in the case of all long-lived species, the same mixing ratios globally. The profiles of odd hydrogen and odd oxygen for the cases of 15 and 0.3μm of H_2O are plotted in Fig. 6. We have assumed the solar zenith angle to be 80°. Such large slant paths reduce the photolyzing and ionizing fluxes for optically thick media such as CO_2, but have little effect on O_3, since the ozone is optically thin. The results are shown in Table III. The increase in ozone predicted is about one-half as great as that observed even after a reduction by 1/5000 in the amount of water vapor. It must be recognized, however, that the results in the table are for a steady state with a sun 10° above the horizon. What is really observed during the early spring on Mars is no doubt a decay of the large quantity of ozone built up during the long polar night.

V. SURFACE SINK

In our "normal" atmosphere the 2μm-atm of ozone predicted is just at the limit of detectability. It should be remarked in this connection, however, that our lower boundary condition of zero flux into the surface is obviously far from realistic in the case of reactive species such as O_3, O, and the odd hydrogen radicals. If in fact we make the extreme assumption that every ozone molecule striking the surface is lost, the flux into the surface is given by

$$\phi(O_3) = -([O_3]/4)[8kT/\pi m(O_3)]^{1/2}. \quad (16)$$

When the distribution of O_3 is that shown in Fig. 1, the flux will be $3.6 \times 10^{13} \text{cm}^{-2}$

sec^{-1}. The total ozone content of the atmosphere (2.04μm-atm) is $5.5 \times 10^{15} \text{cm}^{-2}$ and this flux gives the ozone a lifetime of only a little over 2min. Assuming that every O_3 and every O striking the surface is lost, we have calculated a downward flow of O and O_3, that would change the distributions of O and O_3 in the way shown in Fig. 7 in order to supply the flow into the surface. The result would be to reduce the O_3 content of the atmosphere from 5.5×10^{15} to $1.9 \times 10^{15} \text{cm}^{-2}$, or from 2 to 0.7$\mu$m-atm. However, the $O(^1D)$ production, thence the odd hydrogen production, the supply of O to form OH from HO_2, are all changed in the 20km layer above the surface when these effects are accounted for. On the other hand there will probably be enhanced recombination of CO and O on surface dust grains or aerosols also. Thus it is very likely that surface chemistry as well as gas-phase chemistry plays a very important role in the stability problem, as others (McElroy and Hunten, 1970; Whitten and Sims, 1973) have also pointed out. Note, however, that unless there is an important outgassing of O_2 from the surface, the O_2 production is not seriously enhanced, since the densities are little affected in the region above 20km where most of the O_2 is produced by reaction between O and OH.

To gauge the severity of the problem caused by loss of reactive species upon collision with the Martian surface, we have assumed as an extreme case that the odd hydrogen constituents H, OH, and HO_2 and the odd oxygen components O and O_3 are lost as such upon every collision with the surface. Then we have calculated the distribution that will result, taking into account the loss of $O(^1D)$ production that results from the loss of O_3 near the surface and the consequent reduced production of odd hydrogen. The result are shown in Fig. 7. Two models were tried under the latter assumption. In one, the eddy diffusivity K was assumed to remain at 4×10^8 $\text{cm}^2\text{sec}^{-1}$ all the way to the surface. In the other model, K was allowed to decrease from 4 to $0.7 \times 10^8 \text{cm}^2\text{sec}^{-1}$ in the last 10km, following Gierash and Goody (1968). The latter assumption is essential. When K
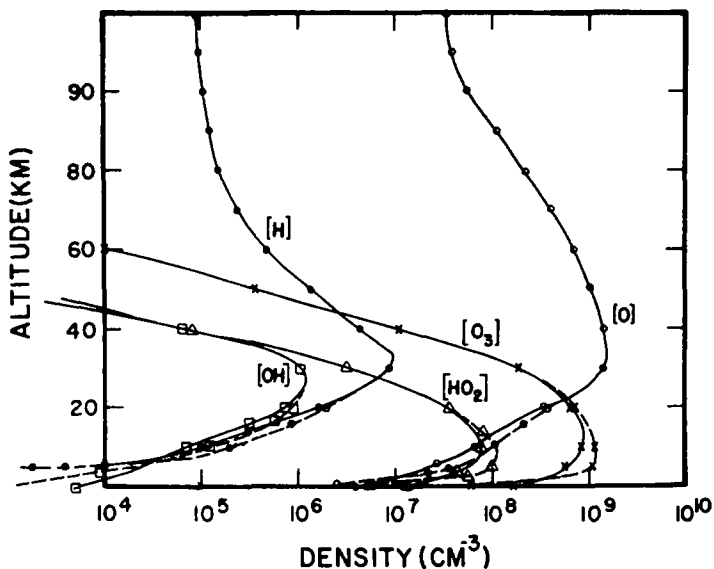
FIG. 7. Density distributions of H, OH, HO_2, O, and O_3 for assumed surface reactions. Solid lines correspond to constant eddy diffusivity $K = 4 \times 10^8 cm^2 sec^{-1}$ and dashed lines correspond to K decreasing from 4 to $0.7 \times 10^8 cm^2 sec^{-1}$ in the 10 km above the surface (Gierash and Goody, 1968).

remains large at all altitudes, the flux of odd oxygen into the surface is 1.1×10^{12} $cm^{-2}sec^{-1}$ out of a total production of $3.6 \times 10^{12} cm^{-2} sec^{-1}$. The flux of odd H is $1.3 \times 10^{11} cm^{-2} sec^{-1}$, while the total production is only $1.9 \times 10^{11} cm^{-2} sec^{-1}$. On the other hand, the surface fluxes of odd oxygen and odd hydrogen drop to 4×10^{11} and $4.5 \times 10^{10} cm^{-2} sec^{-1}$ in the second model.

We have not tried to develop a completely self-consistent model with surface losses accounted for, although there is no problem in doing so mechanically. The problem is that we do not know how to estimate the fraction of H, OH, and HO_2 emerging from the surface as H_2 and H_2O;; the fraction of O and O_3 emerging as O; and the fraction of CO that recombines to CO_2 on the surface. If we leave the mixing ratio of CO at 1.6×10^{-3}, then the amount recombined is only 1.8×10^{12} out of $3.3 \times 10^{12} cm^{-2} sec^{-1}$ produced, because of the decrease in OH density (i.e., the loss of OH to the surface). It would be necessary only to increase the mixing ratio of CO to about 2.9×10^{-3} in order to reestablish a steady state, if we assume no surface re-

combination of CO. This value is still within the limits set by Young (1971), though not if that value is revised to accommodate the data of Tubb and Williams (1972). [The data of Carleton and Traub (1972) indicate a range from 9 to 11×10^{-4} for the volume mixing ratio.] In our opinion, uncertainty with regard to aerosol and surface removal of CO and the other species involved in the chemistry within 10 km of the surface do not allow much significance to be attached to the disparity between the calculated and measured CO mixing ratios under these circumstances.

The ozone abundances are 0.64 and 0.86μm-atm in the two models considered here. Loss of O_3 to the surface puts the total amount in the atmosphere far below the Mariner 9 limit for the "wet" atmosphere.

VI. ARGON IN THE ATMOSPHERE

There has always been some uncertainty regarding the amount of argon that might exist in the Martian atmosphere. The radio occultation results which are composition

dependent are not inconsistent with an argon abundance of 0.20 by volume. Recently, the instruments aboard Mars 6 inferred a gas that could not be exhausted from the mass spectrometer ion pump. This indirect measurement has been interpreted as indicating the presence of several tens of percent of an inert gas, such as argon. This argon inference is consistent with the radiogenic argon model of Levine and Riegler (1974), which predicts about $5 \, g \, cm^{-2}$ of argon corresponding to about 28% of argon by volume (1.8 mbar partial pressure of argon). It appears to be possible that at 6.8 mb pressure level on Mars, the atmosphere may consist of 70% CO_2 and 30% Ar. We have assumed the existence of such an atmosphere and repeated our calculations. One of the principal effect of the presence of argon is to increase the altitude of the exobase for atomic oxygen escape from the dissociative recombination mechanism. When the standard conditions of an O_2 mixing ratio of 1.3×10^{-3} at the surface is assumed and the amount of precipitable water is taken as $20 \mu m$, $[H]_{226}$ taken to be $3.3 \times 10^4 cm^{-3}$, the escape flux of atomic oxygen is found to be $3.5 \times 10^7 cm^{-2} sec^{-1}$. In the case of the argon-rich atmosphere, the exobase for oxygen escape increases to 246 from 226 km. However, the ion densities are higher in the ratio of 1.21 at the same altitude because of the additional ionization of argon and subsequent charge exchange of Ar^+ and CO_2. Thus it appears that the height of the exobase is to a certain extent offset by the increase in recombination rate.

The solution to the coupled flow equations (with no surface loss) is then found to produce an atmosphere with the following characteristics:

$$K = 2.5 \times 10^8 cm^2 sec^{-1},$$
$$[CO]_0 = 2.02 \times 10^{-3}[CO_2]_0,$$
$$[H_2]_0 = 15.5 \, ppm,$$
$$[H_2O_2]_0 = 2 \times 10^9 cm^{-3},$$
$$[H_2]_{226} = 1.63 \times 10^5 cm^{-3},$$
$$\phi_H = 8.7 \times 10^7 cm^{-2} sec^{-1},$$
$$2\phi_{H_2} = 3 \times 10^7 cm^{-2} sec^{-1}$$
$$\int [O]_3 dz = 5 \times 10^{15} cm^{-2} \text{ or } 1.86 \mu m\text{-atm}.$$

The hydrogen escape flux is 1.17×10^8 $cm^{-2} sec^{-1}$ and is not in balance with the oxygen flux. A lower value of K is more tolerable than previously, because the total amount of CO_2 is reduced to 4.8 mb.

If we cut the O_2 mixing ratio to 0.65×10^{-3} but leave the same water vapor, CO_2 and Ar conditions, we find a solution with the following characteristics:

$$[CO]_0 = 2.8 \times 10^{-3}[O_2]_0,$$
$$[H_2]_0 = 40 \, ppm,$$
$$[H_2O_2]_0 = 1.5 \times 10^9 cm^{-3},$$
$$[H]_{226} = 8.4 \times 10^4 cm^{-3},$$
$$[H_2]_{226} = 4.2 \times 10^5 cm^{-3},$$
$$[O_3]dz = 2.8 \times 10^{15} cm^{-2}$$
$$\text{or} \quad 1.04 \mu m\text{-atm}$$
$$\phi_H + 2\phi_{H_2} = 2.2 \times 10^8 + 0.75$$
$$\times 10^8 cm^{-2} sec^{-1}.$$

A reduction in O_2 by a factor of 2 induces an increase in hydrogen escape flux ϕ by a factor of 2.6, an effect almost as large as that in the argon free atmosphere where the change in hydrogen flux was by a factor of 2.9 when the O_2 concentration changed by a factor of 2.

To get the hydrogen escape flux to balance the oxygen escape flux (3.5×10^7 $cm^{-3} sec^{-1}$) the mixing ratio of O_2 is required to be 1.65×10^{-3}, slightly higher than the measured value of 1.3×10^{-3}. We hesitate to cite this imbalance in hydrogen and oxygen escape flux as evidence against a large argon abundance on Mars, in view of the many uncertainties in other measured quantities—exospheric temperature, rate constants such as k_5 and k_7, hydrogen density at the exobase, and the assumption that the hydrogen and oxygen escape rates must balance at all times (that is to say, at present). But there is more than a hint here that the Martian atmosphere would be easier to understand if the ratio of CO_2 to other gases such as Ar were a good deal greater than 7/3.

CONCLUSIONS

Martian photochemistry that recombines CO and O to CO_2 through a water catalytic cycle enables the nonthermal escape of oxygen to govern the thermal

escape of hydrogen. The result is that water escapes from Mars, not hydrogen alone, and there is no pronounced tendency for H of O to accumulate as a result of escape.

ACKNOWLEDGMENTS

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