The Regulation of Hydrogen and Oxygen Escape from Mars

S. C. LIU AND T. M. DONAHUE

Space Physics Research Laboratory, Department of Atmospheric and Oceanic Science,
University of Michigan, Ann Arbor, Michigan 48105

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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 H₂ 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 CO₂ 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 O₂ mixing ratio results and the consequence is to induce a large change in the odd hydrogen concentration, and consequently in H₂ 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 O₂ 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 CO₂ 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 CO₂ undergoes photolysis at a global mean rate of $3 \times 10^{12}\text{cm}^{-2}\text{sec}^{-1}$ (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 O₂ are also low for the atmosphere as a whole, attaining a value of only about $10^{-3}\text{v/v}$. Yet the three-body rate constant for recombination of O with CO is very small, $2 \times 10^{-17}\text{cm}^6\text{sec}^{-1}$, compared to that for formation of O₂ from two oxygen atoms under equivalent conditions, $7 \times 10^{-33}\text{cm}^6\text{sec}^{-1}$. The amount of atomic oxygen in the upper atmosphere can be created by photolysis of CO₂ in about $1.5 \times 10^3\text{sec}$. It has been shown that there is only one viable solution to the problem of maintaining the ratio of atomic oxygen to CO₂ near 135km at a value between $5 \times 10^{-3}$ 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 $10 \times 10^3\text{cm}^2\text{sec}^{-1}$ above 100km if the transport is considered to occur because of eddy diffusion.

But in the lower atmosphere O₂ apparently should form in great amounts even if the oxygen is rapidly removed from the upper atmosphere. The observed amount is $1.3 \times 10^{-3}$ times the CO₂ abundance (Barker, 1972; Carleton and Traub, 1972) and the photolysis rate is $5 \times 10^{10}\text{cm}^{-2}\text{sec}^{-1}$. This gives every O₂ molecule a very long lifetime, about $10^{10}\text{sec}$ 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 O₂ bonds at a rapid rate, to keep the production rate of O₂ to a very low value, or to find a mechanism that combines some measure of both of these properties.

The literature already contains excellent
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 O2 bonds was proposed by Parkinson and Hunten (1972), and it is discussed later in this paper. A solution that essentially short-circuits O2 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 atomic oxygen down to the neighborhood of 30km so rapidly that it has almost no chance of recombining by forming O2 before the radical HO2 begins to be produced in a three-body reaction at a rapid rate. This enables a catalytic cycle to operate efficiently:

\[
\begin{align*}
H + O_2 + M & \rightarrow HO_2 + M, \quad R17, \\
HO_2 + O & \rightarrow OH + O_2, \quad R3, \\
CO + OH & \rightarrow CO_2 + H, \quad R16, \\
Net = CO + O & \rightarrow CO_2. 
\end{align*}
\]

The hydrogen atoms are supplied by dissociation of H2O. The eddy diffusion coefficient required to produce such effective transport has to be greater than \(1.5 \times 10^4\) cm\(^2\)sec\(^{-1}\) at all altitudes above 30km.

Almost all of the O2 in the system is formed by the reaction

\[
O + OH \rightarrow O_2 + H, \quad R2, 
\]

between 25 and 30km. Photolysis of O2 in the Herzberg continuum, occurring mostly between 2 and 15km, is the major sink for O2 although some destruction results from photolysis of H2O2 after its formation from HO2 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 CO2 and to each other. Subsidiary conditions are that the production of H2 from branch (a) of the reaction

\[
\begin{align*}
H + HO_2 & \rightarrow H_2 + O_2, \quad R5, \\
OH + OH & , \quad (b) \\
H_2O + O & , \quad (c)
\end{align*}
\]

be half the thermal (Jeans) escape flux of H atoms and that the formation of H2O from the reaction

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2, \quad R7,
\]

equal the rate of photolysis of 15\(\mu\)m of precipitable water \((5 \times 10^{19} \text{ molecules cm}^{-2})\) (Schorn, 1971; Barker et al., 1970; Conrath et al., 1973). This is to say that water is made at a rate of about \(2 \times 10^9\) molecules cm\(^{-2}\)sec\(^{-1}\). The O3 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 O3 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 \(7 \times 10^7\) 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 \(1.8 \times 10^9\) cm\(^{-2}\)sec\(^{-1}\) would leave behind \(2.4 \times 10^{20}\) molecules cm\(^{-2}\) in 10\(^{13}\)yr. 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 O3 belonging to the H2O which has lost its hydrogen. McElroy’s nonthermal escape mechanism for atomic oxygen is based on the recognition that dissociative recombination of CO2\(^+\) and O2\(^+\) 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 of 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

\[ I_1 = \int k_4[H][HO_2]dz, \]

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 \( O_3 \) concentration and hence a decrease in odd hydrogen. This follows because the integrals

\[ I_2 = \int k_{16}[CO][OH]dz \]
\[ = \int k_{17}[H][O_2][M]dz \]

and

\[ I_3 = \int k_{18}[OH][HO_2]dz \]

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\textsubscript{2} model atmosphere with an exospheric temperature of 320K is assumed (NASA, 1974). The O\textsubscript{2} and precipitable H\textsubscript{2}O abundances are fixed at \(1.3 \times 10^{-3} [\text{CO}_2]\) and 15\textmu m. The density of atomic hydrogen at the exobase, 226km, is fixed at \(3 \times 10^{4} \text{cm}^{-3}\) (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\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, HO\textsubscript{2}, and H\textsubscript{2}.

### TABLE I

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

\(a\) Phillips and Schiff (1962).
\(b\) Clyne and Thrush (1963a).
\(d\) Hochanadel et al. (1972).
\(e\) Schofield (1967).
\(f\) Wilson (1972).
\(g\) Hampson et al. (1973).
\(h\) Clark and Noxon (1972).
\(i\) Bauer et al. (1969).
\(j\) Simonaitis and Heicklen (1972).
\(k\) Stuhl and Niki (1971).
\(l\) Slanger et al. (1972).
\(m\) Fehsenfeld et al. (1969).
\(n\) Fehsenfeld and Ferguson (1972).
\(o\) Walls and Dunn (1974).
\(p\) Bauer (1973).
\(q\) Fehsenfeld et al. (1970).
O$_2$ 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

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

where $\phi_i$, $p_i$, and $l_i$ are local flux, production rates and loss rates for the $i$th atmospheric species. Except for H$_2$O we assume no flux at the surface. The H$_2$O 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 $7 \times 10^{-4}$ to $3.2 \times 10^{-3}$ (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 electron 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$_2$O 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: $1.3 \times 10^{-3}$ and $2.6 \times 10^{-2}$. Solid lines correspond to $1.3 \times 10^{-3}$ O$_2$ mixing ratio and dashed lines correspond to $2.6 \times 10^{-2}$ O$_2$ mixing ratio.](image-url)
neighborhood of 30 to 40 km and the OH density is so high that the production of O₂ by the reaction R2(4) is prohibitively large. Therefore, it is necessary to assume instead (a reasonable assumption after all) that H₂O follows a saturation profile from the surface to 15 km (Hunten and McElroy, 1970). The scale height of this distribution is so small that virtually all the precipitable H₂O is contained below 10 km. The H₂O density at the surface is 6 × 10^{14} cm⁻³, while that at 10 km is fixed at 2 × 10⁸ cm⁻³. Above 15 km the H₂O is assumed to obey the coupled flow equations. The great advantage of this assumption is the H₂O supplies the odd hydrogen precisely where it is needed for the recombination cycle (near the surface) by reaction R13 of H₂O with O(¹D), where the latter species is produced in turn from O₃ photolysis. The odd hydrogen also provides a large source of H₂ at low altitudes (near 25 km) through the reaction branch (5a).

If we assume that the rate constant for this branch of the H, HO, reaction is 3 × 10⁻¹¹ exp(-330/T), as McElroy and Donahue (1972) did, then the H₂ is virtually the sole source of escaping hydrogen atoms, and it supplies them in the ionospheric reactions

\[ \text{CO}_2^+ + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}, \quad \text{R21}, \]  \[ \text{CO}_2\text{H}^+ + e \rightarrow \text{H} + \text{CO}, \quad \text{R22}. \]  

The density of H₂ at the exobase is 1.3 × 10⁵ cm⁻³, larger than that of H by a factor of about 4. However, the effusion velocity of H₂ is so much lower than that of H that twice the escape flux of H₂ is only 24% the escape flux of H. 2φₚ is 2.1 × 10⁷ cm⁻² sec⁻¹ while φₚ × 8.7 × 10⁷ cm⁻² sec⁻¹ and the total hydrogen flux is 1.1 × 10⁸ cm⁻² sec⁻¹. Near 100 km the mixing ratio of H₂ in this scheme is 16 ppm. To account for the L₂ airglow observed by Mariners 6, 7, and 9, Anderson (1973) was obliged to assume a source for atomic hydrogen.

![Graph](image_url)

**Fig. 2.** Density distributions of H₂, H₂O, H₂O₂, and CO for 1.3 × 10⁻³ O₂ mixing ratio. Profiles corresponding to 2.6 × 10⁻³ O₂ mixing ratio can be obtained by shifting these curves linearly according to the ratio listed in Table II.
which required 20 ppm of H₂ in the mesosphere and lower thermosphere. Thus, support is lent to this model by the Lₙ observations.

In Figs. 1 and 2 we show the densities of important species between the surface and 226 km under two assumptions concerning the values of the O₂ 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 × 10⁻³, [O₂]₀ = 1.3 × 10⁻³, [H₂O₂]₀ = 7 × 10⁻⁹, [H₂]₀ = 1.1 × 10⁻⁶ and ∫[H₂O]dz = 5 × 10¹⁹ cm⁻² (15 μm of precipitable water). The abundance of ozone is 5.8 × 10⁻⁵ cm⁻² or 2.15 μm-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 CO₂ since CO₂ is the species that is ionized in the exosphere. The return flux of CO from the exosphere is exactly the CO₂ 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 CO₂⁺ and O₂⁺ 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 90 km because of CO₂ photolysis. Near 30 km both begin to be destroyed through reactions R2, R10, and R16. Molecular oxygen is made just above 30 km by reaction R2 and dissociated in the Harzberg continuum below 15 km and by HO₂ association. H₂O is produced near 33 km as a result of the reaction of the odd hydrogen radicals OH and HO₂ (R7). It is
Fig. 4. Fluxes of odd oxygen (indicated by O) CO, O₂, H₂O₂, and H₂O 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 O₃) below 8km, where it is by far the dominant source of odd hydrogen. It is interesting that the downward flux of H₂O below about 25km and the upward flux of H₂O₂ formed by reacting pairs of HO₂ are almost numerically equal. The flux, −φ(H₂O), is about \(1.7 \times 10^{10}\) cm\(^{-2}\)sec\(^{-1}\) at 10km while \(φ(H₂O₂)\) is \(1.74 \times 10^{10}\) cm\(^{-2}\)sec\(^{-1}\). H₂ is clearly produced at about 25km by the reaction of H and HO₂ (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 CO₂⁺ 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 H₂ still remaining at the exobase and it supports an escape flux of H₂ that amounts to \(2.1 \times 10^7\) 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; \(4 \times 10^8\) cm\(^2\)sec\(^{-1}\) 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 HO₂ in a three-body reaction before they form O₂ in forbiddingly large quantities, but large values of \(K\) are also needed to transport downward rapidly enough the H formed from the reaction of H₂ and CO₂⁺ 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 CO₂⁺, such a large fraction of H₂ 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 H₂ at high altitudes, the bottleneck for escape is at exobase. There is a large upward flux of H₂ to the ionosphere and a large downward flow of H to form H₂ and HO₂ 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 H₂) escape by the nonthermal atomic oxygen escape rate can operate.

The value of the rate constant R5a for H₂ production in the H, HO₂ reaction is $3 \times 10^{-11} \exp(-330/T) \text{cm}^3\text{sec}^{-1}$. 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 O₂ bond is broken after a step of peroxide formation and photolysis added to reactions (1) and (3)

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2, (13) \\
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2(\text{OH}), (14)
\]

amounting to

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2.
\]

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 $k_1$ (a) is no larger than about $3 \times 10^{-12} \text{cm}^3\text{sec}^{-1}$, there is more H₂ formed than may be destroyed by O(1D) and the ion molecule reactions (11) and (12).

III. RELATIONSHIP AMONG O₂ ABUNDANCE, O AND H ESCAPE RATES

We have also performed the exercise of allowing the O₂ mixing ratio to increase from $1.3 \times 10^{-3}$ in stages to $2.6 \times 10^{-3}$. In performing this exercise we keep the CO₂ and H₂O 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 H₂O dissociation and reformation rates must remain unchanged. We find that if we arbitrarily increase the O₂ content of the atmosphere to a new value the H density and H₂ density at the exobase decrease. The factor by which the escape fluxes decrease is, however, always greater than the factor by which the O₂ content of the atmosphere is assumed to increase. Thus if we change the mixing ratio of O₂ from $1.3 \times 10^{-3}$ to $2.6 \times 10^{-3}$, the H density at the exobase goes from $3.1 \times 10^4$ to $1.1 \times 10^4 \text{cm}^{-3}$, and the H₂ density from $1.4 \times 10^5$ to $5.0 \times 10^4 \text{cm}^{-3}$ (Note that H₂ and H decrease by the same factor.) The escape fluxes go to the values

\[
\phi(\text{H}) + 2\phi(\text{H}_2) = 3 \times 10^7 + 7.7 \times 10^6 (15)
\]

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

In Fig. 5 we show the hydrogen fluxes for the case of doubled O₂ abundance. The chain that begins with an increase in O₂ mixing ratio and ends in a decrease in the hydrogen density at the exobase is the following. The ozone abundance grows along with the O₂ abundance because of reaction R20. The result is a doubling in [O₃] and a doubling of the rate of production of O(1D). The lifetime of H₂ against destruction by O(1D) thus is cut in two. Meanwhile the reaction of H with O₂ (R17) causes [H] to decrease and [HO₂] together with [OH] to increase. The effect is to cause a decrease in total H₂ production in the reaction between H and HO₂ (R5). The combined effect of enhanced destruction and diminished production causes the overall decrease in the H₂ density, and consequently the decrease in both H₂ and H density at the exobase, since H is derived from H₂ in the upper atmosphere via the ionosphere reactions R21 and R22.

An increase in the O₂ mixing ratio by 50% to $1.95 \times 10^{-3}$ provokes a decrease in H and H₂ 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, H₂, and CO in response to these large changes in O₂. These changes are
Fig. 5. Fluxes of odd hydrogen (indicated by \( \text{H} \)) \( \text{H}_2 \), \( \text{H}_2\text{O} \), and \( \text{H}_2\text{O}_2 \) for \( 2.6 \times 10^{-3} \text{O}_2 \) mixing ratio. Solid lines indicate upward fluxes and dashed lines indicate downward fluxes.

**TABLE II**

Response of Atmospheric Constituents to Changes in \( \text{O}_2 \) Mixing Ratio

| \([\text{O}_2]_0\) | 1.3 \times 10^{-3} [\text{CO}_2] | 1.95 \times 10^{-3} [\text{CO}_2] | 2.6 \times 10^{-3} [\text{CO}_2] |
| \([\text{CO}]_0\) | 1.6 \times 10^{-3} [\text{CO}_2] | 1.27 \times 10^{-3} [\text{CO}_2] | 1.03 \times 10^{-3} [\text{CO}_2] |
| \([\text{H}_2]_0\) | 1.1 \times 10^{-5} [\text{CO}_2] | 6.1 \times 10^{-6} [\text{CO}_2] | 3.9 \times 10^{-6} [\text{CO}_2] |
| \([\text{H}_2]_{226}\) | 1.4 \times 10^4 \text{cm}^{-3} | 7.9 \times 10^4 \text{cm}^{-3} | 5.0 \times 10^4 |
| \([\text{H}]_{226}\) | 3.1 \times 10^4 \text{cm}^{-3} | 1.77 \times 10^4 | 1.1 \times 10^4 |

summarized in Table II. Naturally the CO mixing ratio must decrease as the \( \text{O}_2 \) mixing ratio increases, because there are relatively more \( \text{HO}_2 \) and \( \text{OH} \) than \( \text{H} \) 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 \( \text{O} \) 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 \( \text{O}_2 \) 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 \( \text{O}_2 \) mixing ratio has a profound effect on the \( \text{H} \) escape flux, since the escape flux changes by a larger factor than the change of the total \( \text{O}_2 \) content of the atmosphere. Therefore,
it may be argued that if in reality the nonthermal 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,
TABLE III
H$_2$O COMPARED TO O$_3$ CONCENTRATION
OVER THE SPRING POLAR CAP

<table>
<thead>
<tr>
<th>H$_2$O</th>
<th>O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µm)</td>
<td>(µm-atm)</td>
</tr>
<tr>
<td>15</td>
<td>0.92</td>
</tr>
<tr>
<td>7.5</td>
<td>1.4</td>
</tr>
<tr>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>0.3</td>
<td>3.9</td>
</tr>
<tr>
<td>3 × 10$^{-3}$</td>
<td>5.2</td>
</tr>
</tbody>
</table>

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$_2$O 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

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

When the distribution of O$_3$ is that shown in Fig. 1, the flux will be $3.6 \times 10^{13}$ cm$^{-2}$ sec$^{-1}$. The total ozone content of the atmosphere (2.04µm-atm) is $5.5 \times 10^{15}$ 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 $5.5 \times 10^{15}$ to $1.9 \times 10^{15}$ cm$^{-2}$, or from 2 to 0.7µm-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 aerols 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 re-action 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 diffusi-vity $K$ was assumed to remain at $4 \times 10^8$ cm$^2$sec$^{-1}$ all the way to the surface. In the other model, $K$ was allowed to decrease from 4 to $0.7 \times 10^8$ cm$^2$sec$^{-1}$ in the last 10km, following Gierash and Goody (1968). The latter assumption is essential. When $K$
remains large at all altitudes, the flux of odd oxygen into the surface is $1.1 \times 10^{12}$ 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 $4 \times 10^{11}$ 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$_2$O; 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 $1.6 \times 10^{-3}$, then the amount recombined is only $1.8 \times 10^{12}$ 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 $2.9 \times 10^{-3}$ in order to reestablish a steady state, if we assume no surface recombination 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 $11 \times 10^{-4}$ 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 0.86 μm-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 5g 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 mbar 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 effects 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 \times 10^{-3} at the surface is assumed and the amount of precipitable water is taken as 20 \mu m, [H\(_{2}\)]_{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:

\[ K = 2.5 \times 10^8 \text{ cm}^2\text{sec}^{-1}, \]
\[ [\text{CO}]_0 = 2.02 \times 10^{-3} [\text{CO}_2]_0, \]
\[ [\text{H}_2]_0 = 15.5 \text{ ppm}, \]
\[ [\text{H}_2\text{O}]_0 = 2 \times 10^9 \text{ cm}^{-3}, \]
\[ [\text{H}]_{226} = 1.63 \times 10^9 \text{ cm}^{-3}, \]
\[ \phi_{\text{H}} = 8.7 \times 10^7 \text{ cm}^2\text{sec}^{-1}, \]
\[ 2\phi_{\text{H}} = 3 \times 10^7 \text{ cm}^2\text{sec}^{-1}, \]
\[ [\text{O}_3] dz = 5 \times 10^{15} \text{ cm}^{-2} \text{ or } 1.86 \mu m\text{-atm} \]

The hydrogen escape flux is 1.17 \times 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 mbar.

If we cut the O\(_2\) mixing ratio to 0.65 \times 10^{-3} but leave the same water vapor, CO\(_2\) and Ar conditions, we find a solution with the following characteristics:

\[ [\text{CO}]_0 = 2.8 \times 10^{-3} [\text{O}_2]_0, \]
\[ [\text{H}_2]_0 = 40 \text{ ppm}, \]
\[ [\text{H}_2\text{O}]_0 = 1.5 \times 10^9 \text{ cm}^{-3}, \]
\[ [\text{H}]_{226} = 8.4 \times 10^4 \text{ cm}^{-3}, \]
\[ [\text{H}_2\text{O}]_{226} = 4.2 \times 10^4 \text{ cm}^{-3}, \]
\[ [\text{O}_3] dz = 2.8 \times 10^{15} \text{ cm}^{-2} \]

or 1.04 \mu m\text{-atm}
\[ \phi_{\text{H}} + 2\phi_{\text{H}_2} = 2.2 \times 10^8 + 0.75 \times 10^8 \text{ cm}^2\text{sec}^{-1}. \]

A reduction in O\(_2\) by a factor of 2 induces an increase in hydrogen escape flux \(\phi\) 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 \times 10^7 cm\(^{-2}\) sec\(^{-1}\)) the mixing ratio of O\(_2\) is required to be 1.65 \times 10^{-3}, slightly higher than the measured value of 1.3 \times 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.

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