The Aeronomy of Hydrogen in the Atmosphere of the Earth

S. C. Liu and T. M. Donahue

The University of Pittsburgh, Pittsburgh, Pa. 15260

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ABSTRACT

The distribution of hydrogen compounds between 50 km and the exobase is calculated subject to the condition that the upward flux of hydrogen atoms be sufficient to supply the thermal escape flux. The effect of varying many parameters, such as exospheric temperature, chemical rate constants, solar UV flux, and atmospheric transport coefficients is explored. It is found that H₂ plays an important role in the chemistry and transport even above 100 km. It is found that the escape flux is determined mainly by the total mixing ratio and relatively insensitive to other factors at exospheric temperatures above 1000K, but is limited by the exobase flow at lower temperatures. A thermal escape flux of 7×10⁻⁶ cm⁻² sec⁻¹ above 1000K is difficult to reconcile with a combined mixing ratio of H₂O, H₂ and CH₄ greater than about 2 ppm at 50 km.

1. Introduction

Since the publication of the classical work of Bates and Nicolet (1950) on the photochemistry of water vapor and its products in the earth's upper atmosphere, it has been clear that somewhere in the mesosphere and stratosphere is the source of the hydrogen that resides in and escapes from the exosphere of the earth. The problem of the flow of hydrogen through the thermosphere and outward from the base of the exosphere has been treated by a number of authors, notably by Mange (1961), Bates and Patterson (1961) and by Kockarts and Nicolet (1962, 1963). In these studies, however, the density of atomic hydrogen was taken as fixed at a lower boundary (100 km), a flux was specified, and no attempt was made to accommodate the contribution of other forms of hydrogen such as H₂ to the flow. The possible presence of important quantities of H₂ in the lower thermosphere has been discussed by several investigators (Bates and Nicolet, 1965; Patterson, 1966; Tinsley, 1969) but no complete quantitative study is available. Donahue (1969) and Brinkman (1969, 1971) both discussed some of the relationships involved but did not develop detailed models.

On the other hand, as Strobel (1972) has emphasized, the numerous attempts to treat the problem of hydrogen in the stratosphere and mesosphere have usually been made without taking into account the flux of hydrogen upward to supply the escape flux. In fact, the status of the aeronomy of the atmospheres of Mars and Venus is better off in this regard than that of earth. Such treatments of the photochemistry as those of McElroy and Donahue (1972) impose as a condition on the production of H₂ in their chemical schemes that the requirements of the hydrogen escape flux be satisfied. For earth, however, there is no definitive and detailed calculation yet published that properly handles the chemistry and transport of hydrogen, oxygen and carbon compounds in the atmosphere as it is related to escape. The consequence is that the important factors controlling the loss of hydrogen from a planet such as earth have not been identified. There has been very little understanding until very recently of the influence of the rate of water photolysis, the strength of eddy transport, variations in the water vapor or methane mixing ratio in the upper stratosphere, or the presence of H₂ at 100 km in the rate of escape of hydrogen. Hunten (1973a, b) has just published two important papers that have gone a long way toward identifying the most important relationships in the problem. In particular, he has emphasized the control exercised by vertical transport near 100 km on the escape flux. He has argued that for a wide range of exospheric temperatures the upward flux is determined by the total mixing ratio of hydrogenic compounds in the lower atmosphere and that it is not sensitive to details of the photochemistry such as the photolysis rate, nor even to the exospheric temperature.

The present paper presents a complete calculation of the photochemistry above 50 km with proper accounting for the escape flux. It supports Hunten's arguments and demonstrates the important role played by molecular hydrogen in providing the upward flux of hydrogen at 100 km. On the other hand, the calculations show that it will be difficult to reconcile present estimates of the escape flux with more than about 2 ppm (by volume) of water vapor at 50 km. Either there are very important ways in which the earth is losing hydrogen other than Jeans escape, or current estimates of mixing ratios for water, H₂ and methane near 50 km are flawed.

While the present paper was being prepared Hunten
Table 1. Reactions and rate constants with references. Where temperature dependences are unknown a $T^0$ dependence of the rate constants was assumed. The rate constants listed are not necessarily exactly those measured by the authors referenced but in some cases represent our evaluation of the consensus of several measurements.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$H + O_2 + M \rightarrow HO + M$</td>
<td>$3.3 \times 10^{-20} \exp(800/T)$</td>
</tr>
<tr>
<td>R2</td>
<td>$H + O_2 \rightarrow OH + O_2$</td>
<td>$2.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>R5</td>
<td>$OH + O \rightarrow OH + H$</td>
<td>$5 \times 10^{-11}$</td>
</tr>
<tr>
<td>R6</td>
<td>$OH + O_2 \rightarrow HO_2 + O_2$</td>
<td>$1.3 \times 10^{-10} \exp(-950/T)$</td>
</tr>
<tr>
<td>R7</td>
<td>$HO_2 + O \rightarrow OH + O_3$</td>
<td>$5 \times 10^{-11}$</td>
</tr>
<tr>
<td>R16</td>
<td>$OH + OH \rightarrow H_2O + O_2$</td>
<td>$2 \times 10^{-12}$</td>
</tr>
<tr>
<td>R17</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$2 \times 10^{-12}$</td>
</tr>
<tr>
<td>R19</td>
<td>$OH + H_2 \rightarrow H_2O + H$</td>
<td>$3.8 \times 10^{-21} \exp(-2600/T)$</td>
</tr>
<tr>
<td>R21</td>
<td>$H + H_2 + M \rightarrow H_3 + M$</td>
<td>$2.6 \times 10^{-20} \exp(375/T)$</td>
</tr>
<tr>
<td>R23</td>
<td>$H + HO_2 \rightarrow H_2O + O$</td>
<td>$3 \times 10^{-11} \exp(-330/T)$</td>
</tr>
<tr>
<td>R24</td>
<td>$H + O_2 \rightarrow H_2O + H$</td>
<td>$7 \times 10^{-11} \exp(-500/T)$</td>
</tr>
<tr>
<td>R27</td>
<td>$HO_2 + HO_2 \rightarrow H_2O + O_2$</td>
<td>$3 \times 10^{-11} \exp(-500/T)$</td>
</tr>
<tr>
<td>R30</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$4.1 \times 10^{-10} \exp(-600/T)$</td>
</tr>
<tr>
<td>R31a</td>
<td>$H_2O_2 + O \rightarrow H_2O + O_2$</td>
<td>$2.3 \times 10^{-10} \exp(-3200/T)$</td>
</tr>
<tr>
<td>R31b</td>
<td>$H_2O_2 + OH \rightarrow H_2O + OH$</td>
<td>$2.3 \times 10^{-10} \exp(-3200/T)$</td>
</tr>
<tr>
<td>Tot.</td>
<td>$OH + CH_4 \rightarrow H_2O + CH_3$</td>
<td>$4.7 \times 10^{-11} \exp(-2500/T)$</td>
</tr>
<tr>
<td>R38</td>
<td>$O + CH_4 \rightarrow OH + CH_3$</td>
<td>$1.2 \times 10^{-10} \exp(-3800/T)$</td>
</tr>
<tr>
<td>R40</td>
<td>$H_2O + CH_4 \rightarrow H_2 + OH + CH_3$</td>
<td>$3 \times 10^{-20}$</td>
</tr>
<tr>
<td>R42</td>
<td>$O + O_2 + CH_4 \rightarrow H_2 + CH_3$</td>
<td>$1.1 \times 10^{-20} \exp(507/T)$</td>
</tr>
<tr>
<td>R51</td>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$1.1 \times 10^{-20} \exp(-2150/T)$</td>
</tr>
<tr>
<td>R52</td>
<td>$O + O_2 + M \rightarrow O_3 + O$</td>
<td>$10^{-5} \sec^{-1}$</td>
</tr>
<tr>
<td>J_{1Ha}</td>
<td>$H_2O + H_2 \rightarrow OH + H$</td>
<td>$7 \times 10^{-5} \sec^{-1}$</td>
</tr>
<tr>
<td>J_{1Hb}</td>
<td>$H_2O + H_2 \rightarrow O + H + O$</td>
<td>$7 \times 10^{-4} \sec^{-1}$</td>
</tr>
<tr>
<td>J_{1Ha}</td>
<td>$H_2O_2 + H_2 \rightarrow O + H + O_2$</td>
<td>$7 \times 10^{-4} \sec^{-1}$</td>
</tr>
<tr>
<td>J_{1Hb}</td>
<td>$H_2O_2 + H_2 \rightarrow O + H + O_2$</td>
<td>$7 \times 10^{-4} \sec^{-1}$</td>
</tr>
<tr>
<td>J_{1Oa}</td>
<td>$O + OH + M \rightarrow O_2 + H + M$</td>
<td>$1 \times 10^{-20} \exp(507/T)$</td>
</tr>
<tr>
<td>J_{1Ob}</td>
<td>$O + O_2 + CH_4 \rightarrow H_2 + CH_3$</td>
<td>$1.1 \times 10^{-20} \exp(-2150/T)$</td>
</tr>
<tr>
<td>J_{1Oa}</td>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$1.1 \times 10^{-20} \exp(507/T)$</td>
</tr>
<tr>
<td>J_{1Ob}</td>
<td>$O + O_2 + M \rightarrow O_3 + O$</td>
<td>$10^{-5} \sec^{-1}$</td>
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<td>J_{1Oa}</td>
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</tr>
<tr>
<td>J_{1Ob}</td>
<td>$O + O_2 + M \rightarrow O_3 + O$</td>
<td>$10^{-5} \sec^{-1}$</td>
</tr>
</tbody>
</table>

References:

and Strobel (1974) have produced a treatment of the problems addressed here. Using rather different computational techniques they have arrives at results for the distribution of constituents with which our calculations will be shown to agree.

2. The coupled flow calculations

The chemical reactions considered in our scheme and their rate constants are shown in Table 1. For a model atmosphere we have adopted the revised U. S. Standard Atmosphere (1966) for July at 45N latitude except for atomic oxygen. We have investigated the effect of varying the atomic oxygen density in the thermosphere because of the continuing uncertainty about the actual value of the density and because of strong indications that the atomic oxygen density at any selected altitude is a highly variable quantity anyway. The atomic oxygen models used are given in Table 2 (Donahue et al., 1973, 1974).

In our coupled flow calculations we have dealt with the following five species: HO, H$_2$, H$_2$O, CH$_4$ and H$_2$O$_2$. Odd hydrogen (HO) can be treated as a single species because the reactions that interconvert H, OH and HO$_2$ are very rapid compared to the rate at which they are created from H$_2$O, H$_2$ or CH$_4$ and reconverted to H$_2$ and H$_2$O. The most important sources of odd hydrogen are photolysis of water vapor, and reaction of O(D)

Table 2. Atomic oxygen densities and photolassociation coefficients of water vapor. The self-consistent [O] below 80 km are photochemical equilibrium values obtained by successive iterations.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>$J_{H_2O}$ (sec$^{-1}$)</th>
<th>High [O] (cm$^{-3}$)</th>
<th>Low [O] (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.2 (8)</td>
<td>2.7 (9)</td>
<td>2.7 (9)</td>
</tr>
<tr>
<td>60</td>
<td>1.3 (8)</td>
<td>5.5 (9)</td>
<td>5.5 (9)</td>
</tr>
<tr>
<td>70</td>
<td>6.0 (8)</td>
<td>7.4 (9)</td>
<td>7.4 (9)</td>
</tr>
<tr>
<td>80</td>
<td>1.4 (8)</td>
<td>1.3 (10)</td>
<td>1.3 (10)</td>
</tr>
<tr>
<td>90</td>
<td>4.0 (8)</td>
<td>2.0 (11)</td>
<td>2.0 (11)</td>
</tr>
<tr>
<td>100</td>
<td>6.2 (8)</td>
<td>3.3 (11)</td>
<td>3.3 (11)</td>
</tr>
<tr>
<td>110</td>
<td>7.6 (8)</td>
<td>4.1 (11)</td>
<td>4.1 (11)</td>
</tr>
<tr>
<td>120</td>
<td>8.5 (8)</td>
<td>4.1 (11)</td>
<td>4.1 (11)</td>
</tr>
<tr>
<td>130</td>
<td>9.4 (8)</td>
<td>3.0 (10)</td>
<td>3.0 (10)</td>
</tr>
<tr>
<td>140</td>
<td>9.7 (8)</td>
<td>1.8 (10)</td>
<td>1.8 (10)</td>
</tr>
</tbody>
</table>

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with water vapor, $H_2$ and $CH_4$. Odd hydrogen is lost mainly by the two reactions

$$H + HO_2 \rightarrow H_2 + O_2,$$

$$OH + HO_2 \rightarrow H_2O + O_2,$$

that convert it to $H_2$ and $H_2O$, and by upward flow at high altitude. An important high-altitude source is reaction of $H_2$ with oxygen atoms in the high-energy tail of the Maxwell-Boltzmann distribution.

In this scheme the apportionment of odd hydrogen among its three dominant forms can be shown to be given by the expressions

$$f_1 = \frac{[H]}{[HO_2]} = \frac{k_1[O]}{k_1[O_2][M]+k_2[O_2]/(k_3[O_2][M]+k_4[O_2])/k_0[O]}$$

$$f_2 = \frac{[OH]}{[HO_2]} = \frac{k_1[O_2][M]+k_2[O_2]}{k_3[O]}$$

while the overall production and loss sets its total concentration through

$$\frac{2f_{12a}[H_2O] + 2k^*[O(1D)][H_2O] + H_2 + 2CH_4}{k_{17}f_2 + k_{23}f_1}$$

in the region below 80 km. Here $k^*$ represents $k_{21}, k_{22}, k_{43}$ as appropriate.

For $O_3$ and $O(1D)$ we calculate photochemical equilibrium values from the relationships

$$[O_3] = \frac{k_{35}[O][O_2][M]}{J_3 + k_{32}[O] + k_{42}[H]}$$

$$[O(1D)] = \frac{J_{35}[O_3][M] + J_{36}[O_2]}{k_0[M]}$$

The effective rate constant for quenching of $O(1D)$ is taken as $5 \times 10^{-11}$ cm$^{-3}$ sec$^{-1}$. The specific rates for photolysis are listed in Table 1. A potentially important source of $H_2$ is the process

$$hv + H_2O \rightarrow H_2 + O_2 (J_{12a}).$$

The wavelength dependence of the cross section for this process is not yet known. There is a band in the absorption cross section of water vapor near 1240 Å and it has been demonstrated that one-fourth of all photons absorbed by $H_2O$ at 1236 Å produce molecular hydrogen in the primary step (McNesby et al., 1962; Welge and Stuhl, 1967). Lacking adequate information on which to base a proper height profile for this process, we have chosen to model a variety of branching ratios for production of the pairs $OH$ and $H$ and $H_2$ and $O$ in the photolysis of water vapor. Obviously the variation in altitude for the one process may be very different than for the other if the branching ratio varies significantly with wavelength. Until better laboratory data are available we choose not to explore the poorly defined range of possible variations and have let the two rates $J_{12a}$ and $J_{13a}$ vary in the identical ways with altitude, i.e.,

$$J_{12a} = f J_{H_2O} \quad \text{and} \quad J_{13a} = (1-f)J_{H_2O}.$$

For each of the five hydrogen species the vertical flux is computed from the standard diffusion equations

$$\phi_i = -D_i\frac{d_i}{dz} \left( \frac{1}{\mathcal{C}_{0i}} \frac{d_i}{dz} + \frac{1}{\mathcal{C}_i} \frac{d_i}{dz} \right)$$

in which eddy diffusion is modeled as analogous to molecular (Fickian) diffusion. Here $\mathcal{C}_i$ is the actual local scale height of the $i$th species, $\mathcal{C}_{0i}$ is $kT_i/(m_i g)$, and $\mathcal{C}_a$ is the local average atmospheric scale height. We have chosen to investigate the effects of various profiles for the eddy diffusion coefficient, but we always let it vary inversely with the square root of the atmospheric density. Following Lindzen (1971), we have chosen to represent $K$ as a function having a maximum at $z_m$ [km]

$$K = K_{100} \exp[0.09(z-100)], \quad z < z_m$$

$$K = K_{100} \exp[0.09(z_m-100)-0.14(z-z_m)], \quad z > z_m,$$

varying as $\rho^{-\frac{1}{2}}$ below $z_m$, and decreasing rapidly above.

We shall have occasion to use three profiles for the eddy diffusion coefficient and we shall refer to them as the low, medium and high values. These are characterized respectively by

$$K_{100} = 5 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}, \quad z_m = 110 \text{ km}$$

$$K_{100} = 1 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}, \quad z_m = 110 \text{ km}$$

$$K_{100} = 3 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}, \quad z_m = 115 \text{ km}$$

The species of interest must also satisfy five continuity equations. Subscripts 1, 2, 3, 4, 5 refer to the
species HO, H₃, H₂O, CH₄, H₂O₂. The most important
terms in the conservation equations are the following:
\[
\frac{\partial \phi_1}{\partial z} + 2k_{17}[\text{OH}][\text{H}_2\text{O}] + 2k_{28}[\text{H}][\text{H}_2\text{O}] + 2k_{29}[\text{HO}_2]^3 \\
= k^*[O^*][2\text{H}_2\text{O} + 2\text{H}_2 + 4\text{CH}_4] \\
+ 2fJ_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + 2k_{29}[\text{CH}_4][\text{OH}] + \cdots, \quad (10)
\]
\[
\frac{\partial \phi_2}{\partial z} + [\text{H}_2][k^*[O^*] + k_{28}[O] + k_{15}[\text{OH}]] \\
= k_{28}[\text{H}][\text{H}_2\text{O}] + (1 - f)J_{\text{H}_2\text{O}}[\text{H}_2\text{O}], \quad (11)
\]
\[
\frac{\partial \phi_3}{\partial z} + [\text{H}_2\text{O}][J_{\text{H}_2\text{O}} + k^*[O^*] + \cdots] \\
= k_{15}[\text{OH}][\text{H}_2\text{O}] + k_{28}[\text{OH}][\text{CH}_4] + \cdots, \quad (12)
\]
\[
\frac{\partial \phi_4}{\partial z} + [\text{CH}_4][J_{\text{CH}_4} + k_{15}[\text{OH}] + \cdots] = 0, \quad (13)
\]
\[
\frac{\partial \phi_5}{\partial z} + [\text{H}_2\text{O}][k_{28}[\text{OH}] + k_{29}[O] + J_{\text{H}_2\text{O}}] \\
= k_{28}[\text{HO}_2]^3, \quad (14)
\]
where O* stands for O(^1D), and the total flux of hydrogen
is automatically conserved, i.e.,
\[
\frac{\partial}{\partial z}(\phi_1 + 2\phi_2 + 2\phi_3 + 4\phi_4 + 2\phi_5) = 0. \quad (15)
\]
Methane burning is modelled in our scheme by
assuming that the conversion of CH₄ to CO₂ starting
with the OH reaction gives two net odd hydrogen. In
other words, we take it that
\[
\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (16)
\]
destroyed one HO, but that consumption of CH₄ pro-
duces 3 HO's (Woosley et al., 1972).
Combination of the five flux equations and the five
continuity equations gives five second-order differential
equations. To obtain solutions for the five species
satisfying these differential equations we need to specify
ten boundary conditions. We have discovered that
the solution of this problem is quite tractable from the
computational standpoint if we try to specify as many
conditions as possible at the upper boundary and then
calculate densities while working downward. We choose
to put the upper boundary at 140 km, except that the
escape flux of hydrogen is specified at the base of the
exosphere and the hydrogen density appropriate to that
flux calculated from the exobase down to 140 km. The
density of atomic hydrogen at 140 km is adjusted at a
later stage in the calculation to accommodate the flux
in the form of H₂ and other species at 140 km. Details
may be found in the Appendix.
Since the specific rate of dissociation of H₂O₂ is
10⁻⁴ sec⁻¹ at 140 km, the density of H₂O₂ is given by
its photochemical equilibrium value and \( \phi_5 \) is set to
zero at 140 km. The fluxes of H₂, H₂O and CH₄ at
140 km can be related to their densities at that altitude
through the relationship
\[
\phi_{i,140} = \int_{140}^{\infty} [i] \lambda d\zeta \quad (16)
\]
\[
= \int_{140}^{\infty} [i] J_{\text{H}_2\text{O}} \exp[(140 - \zeta)/3\zeta] \lambda d\zeta \quad (17)
\]
where \( \lambda_i \) is loss per particle per second. After \( \zeta \) has
been determined these expressions can always be put in the
form
\[
\phi_{i,140} = [i] J_{\text{H}_2\text{O}} \omega_{i,140}, \quad (18)
\]
with \( \omega_{i,140} \) a known quantity. This gives three addi-
tional boundary conditions. Now only three boundary
conditions (i.e., [H₂]₁₄₀, [H₂O]₁₄₀ and [CH₄]₁₄₀) are
left to be specified. It is important to notice that,
although the chemical lifetimes of H₂ and CH₄ at 140
km are only 2.1×10⁸ sec and 1.4×10⁹ sec respectively
due to their reactions with atomic oxygen, it is not
correct to assume photochemical equilibrium for these
species at 140 km. It is true that the conventional
diffusive lifetime of H₂
\[
\tau_D = 3\zeta_{\text{OH}}/D_{\text{H}_2} \quad (19)
\]
is 1.3×10⁹ sec with 3\zeta_{\text{OH}} 210 km and \( D_{\text{H}_2} \) 3.4×10⁸
cm² sec⁻¹. However, the flow is really determined by
the flux equation in the form
\[
\phi_{\text{H}_2}(140) = [\text{H}_2] J_{\text{H}_2\text{O}} \omega_{\text{H}_2,140} \\
= -[\text{H}_2] J_{\text{H}_2\text{O}} D_{\text{H}_2} \left[ \frac{1}{3\zeta_{\text{OH}}} \frac{1 + \tau_D}{3\zeta_{\text{H}_2}} \right] d\zeta. \quad (20)
\]
The proper lifetime is
\[
\tau_D = 3\zeta_{\text{CH}_4}/\omega_{\text{CH}_4,140} \\
= 3\zeta_{\text{H}_2}^2/D_{\text{H}_2}, \quad (21)
\]
and this is only 3×10⁴ sec because the actual scale
height of H₂ is only 10 km. We are not compelled,
therefore, to assume the photochemical equilibrium
values for [H₂] and [CH₄] at 140 km.
The density of CH₄ at 140 km can safely be made
very small since the methane mixing ratio at 50 km
has been measured to be only 0.2 ppm by volume, there
is no recycling of the methane destroyed by O(^1D),
O and OH, and the processes that convert CH₄ to CO
and CO₂ are known to be effective above 50 km. The
value of [CH₄]₁₄₀ is adjusted at a later stage so that
the mixing ratio of CH₄ at 50 km is 0.2 ppm (Ehnhalt
et al., 1972).
Thus, only the quantities [H₂]₁₄₀ and [H₂O]₁₄₀ re-
main to be fixed. It is easy to discover that only a
narrow range is available for the sum of the densities of these two constituents. The reason is that the reaction of oxygen atoms with H$_2$ and photolysis of H$_2$O are the sources of hydrogen atoms above 80 km. If the sum of [H$_2$] and [H$_2$O] is too large, an excess of hydrogen atoms is produced and must be carried downward to form first HO$_2$ and OH and eventually H$_2$ and H$_2$O below 90 km. For each model atmosphere with a specific eddy diffusion coefficient there is a limit on the downward flux that can be tolerated without requiring that the hydrogen density have such a large positive gradient that it becomes impossible to match the density to the photochemical equilibrium values.

The nature of this effect can readily be seen from a simple calculation of the atomic hydrogen flux at 85 km:

$$\phi_H = -D_H \left( \frac{1}{3C_{O,H}} - \frac{1}{3C_{H}} \right) [H] - K \left( \frac{1}{3C_{C}} - \frac{1}{3C_{H}} \right) [H].$$

(22)

Here if $D_H = 10^3$ cm$^2$ s$^{-1}$, $K = 2.5 \times 10^4$ cm$^2$ s$^{-1}$, $3C_{O,H} = 170 \times 10^3$ cm and $3C_{C} = 6 \times 10^3$ cm, then for $[H]$ to be $10^3$ cm$^{-3}$ and $\phi_H$ to be $-5 \times 10^8$ cm$^2$ s$^{-1}$, the actual hydrogen scale height $3C_H$ would need to be 0.78 km. This is an intolerably steep gradient and means that the production of atoms, given by

$$\int_{85}^{140} \left( k_{24}[H_2][O] + J[H_2O] \right) dz,$$

(23)

must be considerably smaller than $5 \times 10^8$ cm$^2$ s$^{-1}$.

On the other hand, if the sum of [H$_2$] and [H$_2$O] is too low at 140 km, the production of hydrogen atoms at high altitude from these species is not adequate to supply the required escape flux. A large positive $\phi_H$ will be needed below 90 km and $[H]$ will be large. The result will be the production of large amounts of H$_2$O and H$_2$ as a result of reactions $k_{17}$ and $k_{28}$. Arguments similar to those just used to put a ceiling on the atomic hydrogen production show that for a given eddy diffusion coefficient there is an upper limit on the amount of H$_2$O and H$_2$ that the system can handle. Hence a lower limit on the sum of [H$_2$] and [H$_2$O] at 140 km is found.

The allowed ratio of [H$_2$] to [H$_2$O] is set by the fact that in the region between about 60 and 80 km the flow of H$_2$O and H$_2$ is in opposite directions, is large, and constitutes virtually the whole hydrogen flow. The balance between [H$_2$] and [H$_2$O] in this region is delicate. [HO] and [H$_2$O$_2$] are in photochemical equilibrium and [CH$_4$] is small. The production and loss of hydrogen atoms is governed by the relationship

$$(p_{H_2} - I_{H_2}) + (p_{H_2O} - I_{H_2O}) = 2e_{H_2}.$$  

(24)

An excess of one species, H$_2$ or H$_2$O, will drive the appropriate loss term up and call up a responding increase in the production term of the other species to maintain the equilibrium. Since the sum of $2\phi_2$ and $2\phi_3$ must equal the escape flux in this region, the ratio of [H$_2$O] to [H$_2$] must be kept carefully adjusted at 140 km, or the upward flow of H$_2$O at 70 km will be out of balance with the downward flow of H$_2$. A search program is used to find the values of [H$_2$] and [H$_2$O] at 140 km that produce a downward flux of H atoms leading to a reasonable profile of [H]—one that joins smoothly to a photochemical equilibrium value at 80 km and balances H$_2$O and H$_2$ fluxes below 80 km. In this process the hydrogen density at 140 km is adjusted so that the atomic hydrogen flux there is equal to the escape flux less twice the H$_2$ flux.

We carry our calculations down to 50 km and stop at that altitude because our ozone chemistry (and O$^1$D production) becomes unrealistic there owing to the absence of odd nitrogen in our reaction schemes (McConnell and McElroy, 1973; McElroy et al., 1974).

The value of [CH$_4$] can be set in this calculation at 140 km at whatever value is desirable (within reasonable limits). Furthermore, very small changes in [H$_2$].$^{14}$O induce large changes in the [H$_2$] profile below 60 km. A large variation in the value of [H$_2$] at 50 km can be produced by changes in [H$_2$].$^{14}$O too small to be significant in the production of H atoms above 80 km or in the H$_2$ flux above 60 km. Hence it is possible to accommodate a fairly large range of possible molecular hydrogen concentrations near 50 km without significantly changing the H$_2$ flow or the H$_2$ density profile above 60 km. Of course, the H$_2$ flux at 50 km is seriously affected by these changes and they perform a corresponding compensating changes in the H$_2$O and CH$_4$ density and flux profiles, but leave the total hydrogen concentration unchanged. The value of [H$_2$].$^{14}$O is adjusted so that the mixing ratio of H$_2$ at 50 km is 0.5 ppm (Scholz et al., 1970).

We have carried out our computations for a wide range of supposed conditions and values of uncertain parameters. As our standard case, we have taken the values of the rate constants indicated in Table 1, set the eddy diffusion coefficient for 100 km at $10^3$ cm$^2$ s$^{-1}$ (the medium value), and set the escape flux at $7 \times 10^8$ cm$^2$ s$^{-1}$. This escape flux is the value according most reasonably with upper atmosphere observations (Donahue, 1966; Vidal-Madjar et al., 1973; Meier and Mange, 1973) of hydrogen density near the critical level. A range of values from 3 to $20 \times 10^8$ cm$^2$ s$^{-1}$ for average exospheric temperatures of 1000K would reasonably accommodate the uncertainties in the various observations, although in our opinion a value greater than $10 \times 10^8$ cm$^2$ s$^{-1}$ is very unlikely. The eddy coefficient value is low enough to assure agreement between observations of the A/N$_2$ ratio and theory (von Zahn, 1970). The rate constant chosen for $k_{17}$ that converts odd hydrogen species OH and HO$_2$ to H$_2$O is much less than the measured value (Hochanadel et al., 1972). The observed value is surprisingly large for such a reaction and we shall discuss the desirable implications of a downward revision in its size. Our
standard value for the rate constant $k_{32}$ of the reaction that converts H and HO$_2$ to H$_2$ is the "large" value preferred by McElroy and Donahue (1972) rather than the one inferred by Hunten and McElroy (1970) from the measurements of Barth and Sues (1960). We shall exercise this rate constant as well as the efficiency for creation of H$_2$ in water photolysis ($f_\text{H}_2\text{O}$) in order to assess the effect on the H$_2$ content of the atmosphere at high altitudes.

3. Results

a. Standard case

In Fig. 1 we show the densities of our principal species as functions of altitude for the standard case.
and an exospheric temperature of 1000K. In Fig. 2 we show the principal source and loss processes as functions of altitude for H2O, H2 and HO, as well as the fluxes of these species. In a study of these results it is apparent that the density of molecular hydrogen is very large near 100 km. The ratio $2[H_2]/[H]$ is 4.64 and $2\phi_{H_2}/\phi_H$ at 100 km is 6.23, $2\phi_2$ being 5.4, and $\phi_H$ being only 1.6 in units of $10^7$ cm$^{-3}$. Much of this H$_2$ is converted to atomic hydrogen below 140 km as a consequence of the reaction with atomic oxygen and the flux at that altitude is of hydrogen mainly in atomic form.

In our models there is a strong flow of H$_2$ up through the 50-km level into a sink resulting from decomposition of H$_2$ by O($^3D$) and OH near 58 km. On the other hand, from the same region (near 59 km) there is a large flux of water vapor created by the reaction R17 of OH and HO$_2$. The water flows upward and downward out of this source. The two forms of odd hydrogen OH and HO$_2$ are concentrated below 80 km. Above that altitude their density decreases rapidly with altitude because the transformation of HO from H to OH and HO$_2$ depends on the presence of O$_2$ and a three-body reaction involving O$_3$. There is an important source of H$_2$ as a result of H and HO$_2$ reaction at 82 km. Out of this source H$_2$ flows upward to be converted to H by atomic oxygen above 125 km and downward to the O($^3D$) sink near 58 km. In the region between 58 and 82 km, where H$_2$ is flowing downward, water vapor is flowing upward from the OH–HO$_2$ source near 58 km to be finally destroyed by photolysis above 82 km. Photodissociation above 82 km gets out of balance with reconversion of odd hydrogen to water vapor. [Note that below 65 km decomposition of H$_2$O by O($^3D$) is the dominant mechanism for destruction of water vapor and production of HO$_2$.] Some of the atomic hydrogen produced from H$_2$O and H$_2$ flows up to the base of the exosphere to escape and some goes back down into the lower atmosphere—to be converted to other forms of odd hydrogen or to recombine with HO$_2$ to form H$_2$. At 90 km the flow of atomic hydrogen reverses. The dominant hydrogenic species between 110 km and 76 km is H$_2$.

One of the most notable results from this calculation is the very low concentration of H$_2$O implied at 50 km by an escape flux of $7\times10^7$ cm$^{-2}$ sec$^{-1}$. The quantity $\sum g_i n_i / n$, where $g_i$ is the number of hydrogen atoms per molecule of species $i$, is only $3.64\times10^{-8}$ at 50 km. As we shall demonstrate and as Hunten (1973b) predicted, the relationship of the total hydrogen mixing ratio to the escape flux of hydrogen when the exospheric temperature is as large as 1000K is quite insensitive to details of chemistry, photolysis rates, or even the efficiency of eddy diffusion transport (within reasonable limits). Hence the mixing ratio of 3.64 ppm for total hydrogen at 50 km, of which (2×0.9) ppm is allotted to H$_2$O, (4×0.2) ppm to CH$_4$ and (2×0.5) ppm to H$_2$, indicates serious problems accommodating water vapor concentrations as large as those measured recently in the stratosphere. Later we shall discuss the effect of varying various atmospheric, environmental or chemical parameters on this deduced mixing ratio. As we shall see, it is not easy to increase it by a significantly large factor.

In Fig. 3 we compare the column density of OH or

\[ L_{\text{OH}} = \int_0^{\infty} [\text{OH}] dz \]  \hspace{1cm} (25)

with the observations of this quantity reported by Anderson (1971a, b). The model profile agrees well with
the observed one. But if \( k_{17} \) is assumed to have its
reported value of \( 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \) (Hochanadel et al.,
1972), the predicted concentration is low by a factor of
about 2.5. From Eqs. (4) and (5) it is clear that the
concentration of OH (like that of HO_2) varies as the
square root of the rate constant \( k_{17} \) in the region 50–70
km where the OH-HO_2 reaction is the dominant sink
for HO. If the mixing ratio for H_2O, H_2 and CH_4 is
larger than the value used here, then a value for \( k_{17} \)
closer to the measured value is consistent with the OH
observations. Because increasing the mixing ratio of
water vapor at 50 km increases the escape flux almost
proportionately when the exospheric temperature is
greater than 900K and it seems very unlikely that the
escape flux is larger than \( 10^8 \text{ cm}^3 \text{ sec}^{-1} \), it seems that
the measured rate constant \( k_{17} \) may be too large by as
much as an order of magnitude. On the other hand, the
rate of production of odd hydrogen involves not only
the concentration of H_2O in this region but the photolysis
rate and the O(1D) concentration. Until all of
these factors are pinned down definitively it will be
premature to draw strong inferences from the OH
discrepancy. We regard it as a very important straw in
the wind, however, suggesting either the need to
accommodate large mixing ratios by finding extra
escape flux or to reduce the rate constant \( k_{17} \). Obviously,
a check on \( k_{17} \) would be most valuable.

The reaction \( k_{23} \) is also important indirectly in
controlling the OH concentration as is apparent from
Eqs. (4) and (5). Use of a small value for \( k_{23} \) (Kaufman,
1964, 1969), i.e.,

\[
k_{23} = 5 \times 10^{-12} T^{1/2} \exp(-1000/T),
\]

along with the smaller value for \( k_{17} \), has the effect
illustrated in Fig. 3.

b. Variation of \( k_{17} \) and \( k_{23} \)

In Figs. 4 and 5 we show the effect of increasing \( k_{17} \)
on the densities, production rates and fluxes of the
principal hydrogenic species. An appreciable reduction
in the role of molecular hydrogen is a consequence of
the reduction in HO_2 density. Reducing \( k_{23} \) as well has
an even more serious effect (Table 4).

Detailed calculations have verified that with all other
parameters remaining fixed the escape flux varies
linearly with the total hydrogen mixing ratio at 50 km.
We have investigated the effect on the escape flux of
varying the exospheric temperature while the total
hydrogen mixing ratio at 50 km remains fixed.

We find, as Hunten predicted (1973b), that the escape
flux is quite insensitive to exospheric temperature
down to about 900K. The density of atomic hydrogen
at the exobase adjusts to the diffusion velocity and keeps
the escape flux almost constant. As Hunten has correctly
divined, as much hydrogen escapes as can flow through
the atmosphere near the 100-km level. The amount of
hydrogen flowing upward is determined by the transport
properties of the atmosphere and the amount of hydro-
gen available. Photochemical details are relatively un-
important so long as the hydrogen is fully converted to
the atomic form below the exosphere.

c. Variation of exospheric temperature

However, below 800K the diffusion velocity becomes
so low that the atomic hydrogen density must become
very large in order to maintain the escape flux. The
density required below 90 km becomes so large that the
sink constituted by reaction R23 becomes very
strong and limits the densities that can be achieved.
(We assume that the total mixing ratio at 50 km re-
mains fixed. Later we shall discuss the time constants in this problem and easily demonstrate that they are long for a change in the total hydrogen concentration at 30 km compared to the times normally involved in variations of the exospheric temperature.) The hydrogen created from photolysis of H$_2$O and the reaction of O with H$_2$ cannot escape very rapidly and most of it begins to flow back down toward the 90-km level to recombine with HO$_2$ and form H$_2$. The atomic and molecular hydrogen density profiles are shown for a large range of assumed exospheric temperatures between 1900K and 500K in Fig. 6. In Fig. 7 we show the dominant production and loss terms along with the fluxes of H, H$_2$ and H$_2$O at 600K. When the exospheric temperature is 600K the odd hydrogen loss rates are considerably enhanced above 85 km. The flux of H is downward at all altitudes below 138 km while the upward flux of H$_2$ is not seriously changed. The result is a

**Fig. 5.** Fluxes and production and loss rates of major species with high $k_d$. The labels are the same as in Fig. 2.

**Fig. 6.** Densities of H and H$_2$ at different exospheric temperatures. H$_2$ densities converge to those of the standard model below 80 km. The mixing ratio of total hydrogen at 50 km is kept constant at 3.64 ppm.
drastically reduced upward flux. This is reflected in a reduced upward flow of H$_2$O and an increased downward flow of H$_2$ near 70 km. The escape flux is only $4.45 \times 10^7$ cm$^{-2}$ sec$^{-1}$. This can be seen in curve 1 of Fig. 8 where the escape flux is plotted as a function of the exospheric temperature. Curves 3, 1 and 0.5 correspond to the high, medium and low eddy coefficients already defined. All curves are normalized by changing the total mixing ratio of hydrogen at 50 km to give $7 \times 10^7$ cm$^{-2}$ sec$^{-1}$ escape flux at 1000K. The total mixing ratios at 50 km are 4.15, 3.63 and 3.53 ppm for respectively low, medium and high eddy diffusion coefficients. The rest of the figure is obtained by maintaining constant total mixing ratio for each eddy diffusion.

When the escape flux drops below $7 \times 10^7$ cm$^{-2}$ sec$^{-1}$ one might expect the total mixing ratio of hydrogen at 50 km to increase due to the constant supply of hydrogen from the earth's surface. However, below 80 km, the total mixing ratio is kept independent of height efficiently (with a time constant 300/K) by eddy diffusion (Hunten, 1973a, b). Increase of the total mixing ratio of hydrogen at 50 km means increase of the total hydrogen column abundance at the same rate. It can be easily shown that it takes millions of years to change the total column hydrogen abundance by 50%. Therefore, one can assume the total hydrogen mixing ratio at 50 km to be constant when the exospheric temperature changes during the present epoch. The standard mixing ratio is selected at 1000K because we feel $7 \times 10^7$ cm$^{-2}$ sec$^{-1}$ is the most likely value for the thermal escape flux and for all practical eddy diffusion models 1000K is high enough to reach the "limiting flux" condition discussed by Hunten (1973a). Using Hunten’s limiting flux formula

$$\phi_i(\tau) = \frac{b_i f_i g}{1 + f_i k T} (m_{av} - m_i),$$

where $b_i = nD_i$, $f_i$ is the mixing ratio of the $i$th species, and $n$ is the total density, we evaluate

$$\phi_i(\text{total H}) = \phi_i(\text{H}) + 2\phi_i(\text{H}_2)$$
Table 3. Huntley’s limiting fluxes at the homopause and exospheric temperatures needed to attain them for the high, medium and low eddy diffusion coefficients.

<table>
<thead>
<tr>
<th>Eddy diffusion</th>
<th>Homopause (km)</th>
<th>Huntley’s limiting flux $\phi_1$ (cm$^{-2}$ sec$^{-1}$)</th>
<th>Effusion velocity required to make $\phi_{ex} = \phi_1$ at exobase (cm sec$^{-1}$)</th>
<th>Corresponding exospheric temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>105</td>
<td>$10.7 \times 10^7$</td>
<td>810</td>
<td>1050</td>
</tr>
<tr>
<td>Medium</td>
<td>95</td>
<td>$7.82 \times 10^7$</td>
<td>590</td>
<td>1015</td>
</tr>
<tr>
<td>Low</td>
<td>90</td>
<td>$7.6 \times 10^7$</td>
<td>570</td>
<td>1010</td>
</tr>
</tbody>
</table>

just above the homopause for each eddy diffusion model. The results are listed in Table 3. The real limiting flux should be a little below the values in Table 3 (Huntley, 1973a). By examining Fig. 8 one can see that the escape flux above 1000K follows exactly the prediction by Huntley. For high effusion velocity the limiting flux at the homopause determines the escape flux. Below 1000K the escape flux is controlled by the effusion velocity at the exobase. The decrease of the escape flux is faster for the higher eddy diffusion model because the limiting flux is larger. One may notice that the decrease in escape flux is not linearly proportional to the decrease of effusion velocity. This can be understood by noticing in Fig. 6 that the hydrogen density at 140 km is higher at the lower exospheric temperature than at the higher temperature. The increase in hydrogen density at the exobase will compensate part of the decrease in escape flux due to the decrease in effusion velocity.

Since all the calculations and discussions above assume steady-state conditions, we must examine the characteristic time constants for one steady state to change to another when the exospheric temperature changes before comparing the results with a real atmosphere. The characteristic time for the hydrogen density when the exospheric temperature decreases is

$$\tau_D = \int_{90 \text{ km}}^{\infty} \frac{[\text{H}]}{\phi_{ex}} dz$$  \hspace{1cm} (28)

(Bates and Patterson, 1961); $\tau_D$ is about 3 days for 2000K, 6 days for 1000K and 100 days for 600K. The characteristic time for the hydrogen density when the exospheric temperature increases is given by

$$\tau_T = \int_{90 \text{ km}}^{\infty} \left( [\text{H}] \frac{T_1 - [\text{H}] T_2}{\phi(x)} \right) dz,$$  \hspace{1cm} (29)

where $T_1$ and $T_2$ are respectively the initial and final exospheric temperatures; $\tau_T$ is about 5 days for $T_1=500K$ and $T_2=600K$, and 10 hr for $T_1=1000K$ and $T_2=1900K$. So, when the exospheric temperature increases, the steady-state hydrogen density at this higher temperature is reached in a few days. Since the refilling process is much slower as the exosphere cools.

Table 4. Some important features for models with different conditions. The escape flux of hydrogen is kept constant at $7 \times 10^7$ cm$^{-2}$ sec$^{-1}$ for all models.

<table>
<thead>
<tr>
<th>$k_{17}$</th>
<th>$k_{23}$</th>
<th>Special conditions</th>
<th>Mixing ratio of total H and $2\text{H}_2$O at 50 km (ppm)</th>
<th>[2H$_2$]/[H] and 2$\phi_1$/3$\phi_1$ at 100 km</th>
<th>[H] at 200 km (cm$^{-2}$)</th>
<th>$\int_{90 \text{ km}}^{\infty}$ [OH] dz (cm$^{-2}$)</th>
<th>[OH] at 50 km and 70 km (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>High</td>
<td>None (standard)</td>
<td>3.64 3.16 3.05</td>
<td>4.64 5.78 (6)</td>
<td>1.26 (13)</td>
<td>1.12 (7)</td>
<td>2.12 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Doubled solar flux</td>
<td>3.45 3.0 3.0</td>
<td>4.9 5.6 (6)</td>
<td>1.5 (13)</td>
<td>1.55 (7)</td>
<td>2.35 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low eddy diffusion</td>
<td>4.15 3.26 2.94</td>
<td>5.97 4.7 (6)</td>
<td>1.29 (13)</td>
<td>1.2 (7)</td>
<td>2.13 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High eddy diffusion</td>
<td>3.55 3.36 3.46</td>
<td>2.67 8.9 (6)</td>
<td>1.31 (13)</td>
<td>1.11 (7)</td>
<td>2.10 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$J_{1 \alpha} = 15% J_{\text{H}_2O}$</td>
<td>3.64 3.16 3.06</td>
<td>5.0 5.5 (6)</td>
<td>1.24 (13)</td>
<td>1.13 (7)</td>
<td>2.02 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$J_{1 \alpha} = 25% J_{\text{H}_2O}$</td>
<td>3.64 3.17 3.07</td>
<td>5.4 5.2 (6)</td>
<td>1.22 (13)</td>
<td>1.13 (7)</td>
<td>1.95 (6)</td>
</tr>
<tr>
<td>Low</td>
<td></td>
<td>None</td>
<td>3.16 2.66 2.72</td>
<td>1.12 0.98</td>
<td>1.3 (7)</td>
<td>1.42 (13)</td>
<td>1.07 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>3.86 3.37 3.0</td>
<td>2.65 8.5 (6)</td>
<td>6.26 (12)</td>
<td>4.6 (6)</td>
<td>1.2 (6)</td>
</tr>
<tr>
<td>Low</td>
<td></td>
<td>None</td>
<td>3.8 3.3 2.82</td>
<td>0.82 0.68</td>
<td>1.48 (7)</td>
<td>6.6 (12)</td>
<td>1.3 (6)</td>
</tr>
</tbody>
</table>
down, we expect that the real hydrogen density distribution will reflect the 1000K or higher temperature most of the time. And unless the exospheric temperature remains at 600K for about one-third of a year during solar minimum, the steady state of 600K will never be reached.

d. Variation in eddy diffusion coefficient

Reducing the eddy diffusion coefficient will lead to an increased gradient in the total hydrogen mixing ratio in the region where the flow is controlled by turbulence and compel a larger mixing ratio at 50 km to be associated with a specific upward flux. This is the case when limiting diffusion is dominant. The effect is illustrated in Table 4 where we show mixing ratios for all hydrogen and for water vapor at 50, 70 and 90 km and various values of eddy diffusion coefficient at 100 km. The expected change does occur but only results in about a 12% increase at 50 km when the eddy coefficient is reduced by a factor of 2 from 1 to $0.5 \times 10^6$ cm$^3$ sec$^{-1}$ at 100 km.

The distribution of species above 90 km reflects the fact that a given amount of atomic hydrogen produced from H$_2$ and H$_2$O dissociation is transported with more difficulty downward when the eddy diffusion coefficient is reduced. We have also investigated the effect of placing the eddy diffusion coefficient maximum at 115 km where the OGO-6 airglow results of Donahue et al. (1973) suggest that it should be located but because of the dominance of molecular diffusion above 100 km the effects produced are insignificant.

It is a paradox, apparent in Fig. 8, that at exosphere temperatures below those at which the transition from limiting diffusion control to effusive flow control has occurred, increasing the eddy diffusion coefficient causes a decrease in escape flux. All other properties of the problem remaining fixed. Thus at 600K, with the mixing ratio held at 50 km to 3.63 ppm the total flux
drops from 6.2 to 4.5 to 2 as $K$ increases from 0.5 to 1 to $3 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$ at 100 km. The statement of the paradox is that increasing the efficiency of transport reduces the net upward flux. Since the transition from limiting diffusion depends on the ratio of $w_e$ to $K/\beta \alpha$, where $w_e$ is the effusion velocity at the exobase, we understand how this situation is created. Inspection of Figs. 9a and 9b where densities and fluxes are plotted for the three different values of $K$ and an exospheric temperature of 600K shows clearly the reason for the effect. The shutting off of the diffusive flow is accompanied by an increase in the altitude of the sink for H that remains at 90 km at high exospheric temperatures. The altitude at which the H flow reverses decreases with exospheric temperature. The direction of H flow becomes downward in the region where $K$ is important. Increasing $K$ has the effect of increasing the downward flux of atomic hydrogen to intolerably large values.
unless the density of H decreases above 90 km. The decrease in density there propagates all the way to the exobase and the escape flux is diminished.

In this regime the situation is rather analogous to the case of O and O in the same altitude range where O flows upward to be dissociated and atoms flow downward to recombine. Increasing $K$ is accompanied by a decrease in [O] as long as the photolysis rate is fixed. By analogy here H$_2$O flows upward through the 90-km level to be photolysed and H$_2$ flows upward to be dissociated by atomic oxygen atoms. This flow is balanced by the atomic hydrogen flow downward. Flow reversal eventually occurs but at a very much higher altitude. Note that when $K$ is $3 \times 10^6$ cm$^2$ sec$^{-1}$ there is an appreciable flux of H$_2$O even at 100 km.

e. Variation of solar flux

It has often been suggested that the intensity of the flux of solar radiation capable of dissociating H$_2$O would control the supply of hydrogen atoms available or escape and hence the escape flux. According to the ideas of Hunten and the effects we have just discussed this is not so. The mixing ratio and the transport properties of the atmosphere are controlling. We have verified this fact by arbitrarily doubling the solar UV flux, i.e., by doubling all specific dissociation rates (but keeping everything else, including exospheric temperature, constant). The escape flux for an exospheric temperature of 1000K changed only from 7 to 7.2 cm$^{-3}$ sec$^{-1}$. As can be seen in Figs. 10 and 11 where constituent densities, production and loss rates, and fluxes are plotted, the increased solar flux consumes the water vapor seriously below about 85 km where the photolysis rate is much higher in the doubled flux case. However, the reduced density at this altitude results in an almost order-of-magnitude reduction in H$_2$O density at the 100-km level. The result is that the production of odd hydrogen through photolysis of H$_2$O is considerably reduced above 85 km. The flux of atoms upward is actually smaller. On the other hand, the enhanced densities of odd hydrogen below 85 km lead to enhanced H$_2$ production and there is a compensating upward flux of H$_2$.

In Figs. 12–14 we show the effects produced by decreasing the solar flux arbitrarily by a factor of 3. The exercise resulting in these figures was performed for the high value of $k_{17}$, so that the mixing ratio for total hydrogen was 3.85 ppm at 50 km for an escape flux of $7 \times 10^7$ cm$^{-2}$ sec$^{-1}$. Reducing the solar flux drives the mixing ratio up to 4.94 ppm if we keep the escape flux fixed, or reduces the escape flux to $5.6 \times 10^7$ cm$^{-2}$ sec$^{-1}$ if we hold the initial mixing ratio at 3.85 ppm. In the figures we see that the reduction in flux occurs because the upward H$_2$ flux is drastically reduced above the source at 83 km. The production of odd hydrogen and hence the densities of H and HO$_2$ are seriously reduced in the neighborhood of this source. Since the destruction rate of H$_2$ is negligibly small in this region the effect is to reduce the H$_2$ source. On the other hand, it will be noted that despite the reduction in the source of H$_2$O through $k_{17}$ there is an enhancement of the H$_2$O flux above 85 km. This is because the destruction of H$_2$O by photolysis is important in the region above 75 km and the reduction in UV dissociating flux is more important than the reduction in H$_2$O production.

In Table 6 we summarize the effects of varying the solar flux. A factor of 3 reduction in the UV intensity causes a 28% change in escape flux if $k_{17}$ is large, but a
Fig. 13. Comparison of fluxes for the two models described in Fig. 12. The solid lines are for the model with normal solar flux and the dashed lines for the model with one-third solar flux. The arrow indicates the direction of flow.

Fig. 14. Comparison of major production of $H_2(k_B[H][H_2O])$, major production of $H_2O(k_B[OH][H_2O])$, and major losses of $H_2O (j_{Reco}[H_2O]$ and $k^*[O^*][H_2O])$ for the two models described in Fig. 12. The solid lines are for the model with normal solar flux and the dashed lines for the model with one-third solar flux.
doubling of the UV source only produces a 6% increase in escape flux if $k_{17}$ is small.

f. Variation of other parameters

The results obtained by varying other parameters are also summarized in Tables 4 and 5. Changing the atomic oxygen density profile has little effect except to change the amount of $H_2$ allowed at high altitude. As expected, larger atomic oxygen densities lead to lower $H_2$ densities. Increasing the amount of $H_2$ produced in photolysis increases the amount of $H_2$ at high altitude. A change from 5.7 to 23% in the fraction of all photolysis events leading directly to $H_2$ does not change the escape flux. It changes the $[H_2]/[H]$ ratio at 100 km by 16% and the values of $[H_2]$ at 100 km by 4% (the atomic hydrogen density decreases). This is for the "large" value of $k_{23}$, the "low" $k_{17}$ and a total hydrogen mixing ratio of 3.64 ppm at 50 km. Clearly reducing $k_{23}$ and reducing the $H_2/OH$ branching ratio would reduce the role of $H_2$ significantly.

4. Discussion

The results reported here constitute confirmation of the general predictions of Hunt (1973b) that so-called limiting flux controls the escape of hydrogen from earth when the exospheric temperature is high enough. They also are in fairly good agreement with the results obtained in a similar coupled flow calculation recently completed by Hunt and Strobel (1974). There is little point in our repeating here all of the discussion that appears in their paper. We refer the reader to the discussion there of such matters as the present status of $H_2O$, $OH$ and $H_2$ measurements in the stratosphere and factors affecting the value taken for the Jans escape flux. Measured $H_2O$ concentrations are in the range 3-10 ppm (6-20 ppm for total hydrogen) near our lower boundary.

We would take a somewhat stronger position in this paper than Hunt and Strobel took with regard to the conflict between the lower atmosphere measurements and the amount of Jans escape. It seems to us that a rather serious discrepancy exists and that we must either call into question the stratospheric measurements or find some additional mechanism for draining large quantities of hydrogen away from the earth. The discrepancy is between our requirement for about 4 ppm total hydrogen at 50 km when the exospheric temperature is above 900K and measured values in the range 8-22 ppm. As we have pointed out a careful study of the factors affecting the $OH$ distribution below 80 km, and particularly the value of $k_{17}$, may be very rewarding in resolving some part of this conflict.

The most recently published seasonal data—those obtained by Blamont et al. (1974) from the D2A satellite—give both density and temperature at the

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**Table 5.** Some important features for models with different exospheric temperatures using high [O], high $k_{23}$ and low $k_{17}$. The total mixing ratio of hydrogen at 50 km is kept constant at 3.64 ppm by changing the escape flux of hydrogen.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Escape flux (10^7 cm^-4 sec^-1)</th>
<th>Mixing ratio of total H and 2H_2O at 50 km (ppm)</th>
<th>Mixing ratio of total H and 2H_2O at 70 km (ppm)</th>
<th>Mixing ratio of total H and 2H_2O at 90 km (ppm)</th>
<th>2[H_2]/[H] at 100 km</th>
<th>2φH at 100 km</th>
<th>[H] at 100 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.06</td>
<td>3.64</td>
<td>3.74</td>
<td>5.93</td>
<td>0.57</td>
<td>8.1×10^7</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>4.4</td>
<td>3.64</td>
<td>3.41</td>
<td>4.31</td>
<td>0.157</td>
<td>3.9×10^7</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>6.3</td>
<td>3.66</td>
<td>3.25</td>
<td>0.13</td>
<td>2.42</td>
<td>1.5×10^7</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>7</td>
<td>3.63</td>
<td>3.16</td>
<td>3.05</td>
<td>6.4</td>
<td>5.8×10^6</td>
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</tr>
<tr>
<td>1900</td>
<td>7.05</td>
<td>3.63</td>
<td>3.15</td>
<td>3.02</td>
<td>6.0</td>
<td>5.4×10^6</td>
<td></td>
</tr>
</tbody>
</table>

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**Table 6.** Effects of changing solar UV flux. The escape flux of hydrogen is kept constant at 7×10^7 cm^-4 sec^-1.

<table>
<thead>
<tr>
<th>$k_{17}$</th>
<th>Solar flux</th>
<th>Mixing ratio of total H at 50 km (ppm)</th>
<th>Change of mixing ratio compared with normal</th>
<th>2[H_2]/[H] at 100 km</th>
<th>2φH at 100 km</th>
<th>[H] at 100 km (cm^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
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<td>High</td>
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</tbody>
</table>
critical level. Taking the extremes of the error bars published by these authors we find the escape flux on 27 April 1971 to vary from $(3.58 \pm 3.20) \times 10^7$ cm$^{-2}$ s$^{-1}$ at 0000 local time to $(3.20 \pm 2.07) \times 10^7$ cm$^{-2}$ s$^{-1}$ at 1600. If we take the temperature measured by incoherent scatter for that day rather than the satellite experiment and calculate an effusion velocity to combine with the measured density, the situation is somewhat improved. The escape flux varies from $(1.7 \pm 0.44) \times 10^7$ cm$^{-2}$ s$^{-1}$ to $(3.2 \pm 0.1) \times 10^7$ cm$^{-2}$ s$^{-1}$.

We feel that $10 \times 10^7$ cm$^{-2}$ s$^{-1}$ is probably too generous an estimate for the Jeans escape flux above 1000K. For the extreme case of very low solar flux and large $kT$ in our calculations the total hydrogen mixing ratio at 50 km is only 7.15 ppm, still somewhat below the "low" measured value of 8 ppm.

Many other exercises remain to be carried out using the techniques described here before the results can be applied in detail to the real atmosphere. To test the general conclusions a measurement of the H and H$_2$ distribution between 90 and 150 km would be most interesting.

Acknowledgments. For indispensable advice concerning chemical rate constants and general helpfulness we wish to thank J. Anderson and F. Kaufman. We have also benefitted from several illuminating discussions with D. M. Hunten, M. B. McElroy, Nien Dak Sze and S. Wofsy. This work was supported, in part, by ARPA (DA-BCO-473-C0037) and the National Science Foundation, Atmospheric Sciences Station, under Grant GA-37744.

APPENDIX

Numerical Method for Solving the Diffusion and Continuity Equations

The diffusion equation is cast in the form

$$
\phi_i = -D_i n_e \frac{d}{dz} \left[ \frac{n_i(z)}{n_e(z)} \right] - K n_e \frac{d}{dz} \left[ \frac{n_i(z)}{n(z)} \right],
$$

(A1)

where we use the symbols $n_i$ and $n$ in place of $[I]$ and $[M]$ to avoid cumbersome notation; $n$ is the total atmospheric density and $n_i(z)$ the "diffusive equilibrium" density. These quantities satisfy respectively the equations

$$
1 \frac{dn(z)}{dz} + \frac{1}{n(z)} \int_{z}^{z+\Delta z} dz' \frac{dn(z')}{dz'} = 0,
$$

(A2)

$$
1 \frac{dn_i(z)}{dz} + \frac{1}{n_i(z)} \int_{z}^{z+\Delta z} dz' \frac{dn_i(z')}{dz'} = 0.
$$

(A3)

In terms of a small altitude interval $\Delta z$ the diffusion equation (A1) can be expressed as a difference equation

$$
\phi_i = - \frac{D_i n_e}{\Delta z} \Delta \left( \frac{n_i}{n_e} \right) - \frac{K n}{\Delta z} \Delta \left( \frac{n_i}{n} \right),
$$

(A4)

where $\phi_i$, $D_i$, $n_e$, $K$ and $n$ are the average values of these quantities in the altitude interval between $z$ and $z+\Delta z$. Thus, for small $\Delta z$,

$$
\phi_i = \frac{\phi_i(z+\Delta z) + \phi_i(z)}{2},
$$

(A5)

$$
n_e(z+\Delta z/2) = n_e(z+\Delta z) / 2,
$$

(A6)

$$
n_e(z+\Delta z/2) = n_e(z+\Delta z) / 2,
$$

(A7)

$$
\Delta \left( \frac{n_i}{n_e} \right) / n_e = \left[ \frac{n_i(z+\Delta z)}{n_e(z+\Delta z)} - \frac{n_i(z)}{n_e(z)} \right] / n_e(z).
$$

(A8)

Substitution for these quantities in (A4) leads to the following form for the diffusion equation:

$$
\phi_i(z+\Delta z) + \phi_i(z) = \frac{2D_i n_e(z+\Delta z/2)}{\Delta z} \left[ \frac{n_i(z+\Delta z)}{n_e(z+\Delta z)} - \frac{n_i(z)}{n_e(z)} \right] - \frac{2K n(z+\Delta z/2)}{\Delta z} \left[ \frac{n(z+\Delta z)}{n(z)} - \frac{n(z)}{n(z)} \right].
$$

(A9)

The integrals of (A2) and (A3) give $n_e$ and $n$ in terms of known functions of $z$ and permit the ratios appearing in (A9) to be cast in the form

$$
A_i = \frac{n_e(z+\Delta z/2)}{n_e(z+\Delta z/2)} = \left[ \frac{T(z+\Delta z/2)}{T(z+\Delta z/2)} \right]^{1+\alpha} \exp \left[ \frac{-\Delta z}{2K_c(z+\Delta z/4)} \right],
$$

where the integral in the exponential has been approximated as

$$
\int_{z+\Delta z/2}^{z+\Delta z} dz' \frac{1}{3K_c(z')} = \frac{\Delta z}{2K_c(z+3\Delta z/4)},
$$

$$
B_i = \frac{n_e(z+\Delta z/2)}{n_e(z)} = \left[ \frac{T(z)}{T(z+\Delta z/2)} \right]^{1+\alpha} \exp \left[ \frac{-\Delta z}{2K_c(z+\Delta z/4)} \right],
$$

$$
E_i = \frac{n(z+\Delta z/2)}{n(z+\Delta z/2)} = \left[ \frac{T(z+\Delta z/2)}{T(z+\Delta z/2)} \right]^{1+\alpha} \exp \left[ \frac{-\Delta z}{2K_c(z+3\Delta z/4)} \right],
$$

$$
F_i = \frac{n(z+\Delta z/2)}{n(z)} = \left[ \frac{T(z)}{T(z+\Delta z/2)} \right]^{1+\alpha} \exp \left[ \frac{-\Delta z}{2K_c(z+\Delta z/4)} \right].
$$
In terms of the quantities $A_i$, $B_i$, $F$ and $E$, (A9) may be expressed as
\[
\phi(z+\Delta z) + \phi_i(z) = \frac{2D_i}{\Delta z} [A_i n_i(z+\Delta z) - B_i n_i(z)] - \frac{2K_i}{\Delta z} [E n_i(z+\Delta z) - F n_i(z)]. \tag{A10}
\]

In the present calculation (A10) represents five equations for the ten quantities $\phi_i(z+\Delta z)$ and $n_i(z+\Delta z)$ in terms of $\phi_i(z)$ and $n_i(z)$.

As for the continuity equations, they may be written, for finite $\Delta z$, in the form
\[
\phi_i(z+\Delta z) - \phi_i(z) + \left[\bar{\nu}_i(z) - p_i(z)\right] \Delta z = 0. \tag{A11}
\]

In evaluating the average production and loss terms it is important not to disturb the conservation condition (15). Terms in $\bar{\nu}_i$ and $p_i$ like
\[
\bar{k}_w n_i^2 \quad \text{and} \quad \bar{k}_u n_i n_j
\]
are linearized as follows:
\[
\bar{k}_w n_i^2 = k_w (z+\Delta z/2) n_i(z+\Delta z), \quad \bar{k}_u n_i n_j = \frac{1}{2} k_u (z+\Delta z/2) \times [n_i(z)n_j(z+\Delta z) + n_i(z+\Delta z)n_j(z)]. \tag{A12}
\]

After these approximations are made Eqs. (A11) become five linear equations for $\phi_i(z+\Delta z)$ and $n_i(z+\Delta z)$ in terms of $\phi_i(z)$ and $n_i(z)$. Together the linearized set (A11) and (A9) of ten equations can be solved for $n_i(z+\Delta z)$ and $\phi_i(z+\Delta z)$.

In practice, the computations are developed downward from the 140-km level in steps of 0.2 km for $\Delta z$. The adequacy of the step size has been tested by running some calculations with $\Delta z$ equal to 0.1 km. The total hydrogen mixing ratios obtained at 50 km for the two cases differ by less than 0.1%. The fluxes and species densities differ by less than 1%. The step size of 0.2 km has therefore been judged to be small enough for results as accurate as desired.

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