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ON THE PHOTOCHEMISTRY OF OZONE IN THE OZONE LAYER

By
Eigil Hesstvedt

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Summary. On the basis of a photochemical model number densities of $O(^1D)$, $O(^3P)$, O_3, OH, HO_2, H_2, H_2O, H_2O_2 and H are computed for heights from 15 to 40 km. The model is modified by considering vertical eddy transport ($K_z = 4 \times 10^8$ cm^2/s). It is shown that molecular hydrogen is transported from the troposphere to about 35 km without being broken down. Also H_2O_2 and O_3 are affected by eddy motion in the 15—25 km region. Good agreement is obtained between theoretical and observed number densities of ozone.

1. Introduction. Our understanding of the photochemistry of the ozone layer was considerably improved when hydrogen was introduced in the photochemical model (Hunt, 1966). However, the agreement between theoretical and observed ozone densities is not yet satisfactory. It is generally believed that the main reason for this is the incomplete knowledge of many of the reaction rates used in the photochemical model. But it is also obvious that atmospheric transport processes will modify the theoretical values, especially in middle and high latitudes.

In the present paper a recomputation is made of theoretical ozone densities by using recent values for the parameters. The effect of vertical eddy transport will also be evaluated. Finally it will be shown how the theoretical ozone profile is influenced by variations in the parameters.

2. Reaction scheme. The reactions used in the present model are, with a few exceptions, the same as those used by Hunt (1966) and Hesstvedt (1968).

(1) $O(^3P) + O(^3P) + M \rightarrow O_2 + M$ $k_1 = 2.7 \times 10^{-33}$ (Reeves, Mañella and Harteck, 1960)

(2) $O(^3P) + O_2 + M \rightarrow O_3 + M$ $k_2 = 8.2 \times 10^{-35} \exp(890/RT)$ (Benson and Axworthy, 1965)

(3)	$O(^3P)+O_3\rightarrow 2O_2$	$k_3=8\times10^{-12}\exp(-3260/RT)$ (CAMPBELL and NUDELMAN, 1960)
(4a)	$O_2+h\nu\rightarrow O(^3P)+O(^3P)$	J_{2a} $(1750A<\lambda<2424A)$ $\}$ $J_{2a}+J_{2b}=J_2$
(4b)	$O_2+h\nu\rightarrow O(^3P)+O(^1D)$	J_{2b} $(\lambda<1750A)$ $\}$
(5a)	$O_3+h\nu\rightarrow O(^3P)+O_2$	J_{3a} $(\lambda>3100A)$ $\}$ $J_{3a}+J_{3b}=J_3$
(5b)	$O_3+h\nu\rightarrow O(^1D)+O_2$	J_{3b} $(\lambda<3100A)$ $\}$
(6)	$OH+O(^3P)\rightarrow H+O_2$	$k_6=5\times10^{-11}$ (KAUFMAN, 1964)
(7)	$HO_2+O(^3P)\rightarrow OH+O_2$	$k_7=10^{-11}$ (KAUFMAN, 1964)
(8)	$H+O_2+M\rightarrow HO_2+M$	$k_8=7.4\times10^{-32}$ (LARKIN and THRUSH, 1964)
(9)	$H+O_3\rightarrow OH+O_2$	$k_9=2.6\times10^{-11}$ (KAUFMAN, 1964)
(10)	$OH+HO_2\rightarrow H_2O+O_2$	$k_{10}=10^{-11}$ (KAUFMAN, 1964)
(11)	$H_2O_2+h\nu\rightarrow 2OH$	$J_{H_2O_2}$ $(1875A<\lambda<3825A)$
(12)	$O(^3P)+H_2O_2\rightarrow OH+HO_2$	$k_{12}=10^{-15}$ (FONER and HUDSON, 1962)
(13)	$HO_2+HO_2\rightarrow H_2O_2+O_2$	$k_{13}=3\times10^{-12}$ (KAUFMAN, 1964)
(14)	$OH+H_2O_2\rightarrow H_2O+HO_2$	$k_{14}=4\times10^{-13}$ (FONER and HUDSON, 1962)
(15)	$OH+OH\rightarrow H_2O+O(^3P)$	$k_{15}=2.8\times10^{-12}$ (KAUFMAN, 1964)
(16)	$H_2O+h\nu\rightarrow OH+H$	J_{H_2O} $(1350A<\lambda<2375A+Ly\alpha)$
(17)	$O(^1D)+H_2O\rightarrow 2OH$	$k_{17}=10^{-11}$ (HUNT, 1966)
(18)	$H+HO_2\rightarrow H_2+O_2$	$k_{18}=2\times10^{-13}$ (CLYNE and THRUSH, 1963)
(19)	$H_2+OH\rightarrow H_2O+H$	$k_{19}=10^{-10}\exp(-5900/RT)$ (KAUFMAN, 1964)
(20)	$O(^1D)+M\rightarrow O(^3P)+M$	$k_{20}=10^{-10}$ for $M=O_2$ (SCHIFF)
		$k_{20}=2.2\times10^{-11}$ for $M=N_2$ (DE MORE and RAPER, 1964)
(21)	$O(^1D)+H_2\rightarrow OH+H$	$k_{21}=10^{-11}$ (HUNT, 1966)
(22)	$O(^3P)+H_2\rightarrow OH+H$	$k_{22}=4.1\times10^{-11}\exp(-7700/RT)$ (FENIMORE and JONES, 1958)
(23)	$HO_2+O_3\rightarrow OH+2O_2$	$k_{23}=10^{-14}$ (HUNT, 1966)
(24)	$OH+O_3\rightarrow HO_2+O_2$	$k_{24}=5\times10^{-13}$ (KAUFMAN, 1964)
(25)	$H+H_2O_2\rightarrow H_2+HO_2$	$k_{25}=10^{-13}$ (FONER and HUDSON, 1962)
(26)	$HO_2+h\nu\rightarrow OH+O(^3P)$	J_{HO_2}
(27)	$H+OH\rightarrow H_2+O(^3P)$	$k_{27}=1.8\times10^{-11}\exp(-5800/RT)$ (KAUFMAN, 1964)
(28)	$H+O_2\rightarrow OH+O(^3P)$	$k_{28}=1\times10^{-9}\exp(-16800/RT)$ (KAUFMAN, 1964)
(29)	$H+O_3\rightarrow HO_2+O(^3P)$	$k_{29}=2\times10^{-10}\exp(-4000/RT)$ (BATES and NICOLET, 1950)
(30)	$H+HO_2\rightarrow 2OH$	$k_{30}=10^{-11}$ (KAUFMAN, 1964)
(31)	$H+OH+M\rightarrow H_2O+M$	$k_{31}=2.5\times10^{-31}$ (KAUFMAN, 1964)
(32)	$O(^3P)+OH+M\rightarrow HO_2+M$	$k_{32}=1.4\times10^{-31}$ (PETERSEN and KRETSCHMER, 1960)
(33)	$H+HO_2\rightarrow H_2O+O(^3P)$	$k_{33}=2\times10^{-10}\exp(-4000/RT)$ (BATES and NICOLET, 1950)
(34)	$H+H+M\rightarrow H_2+M$	$k_{34}=2.6\times10^{-32}$ (LARKIN and THRUSH, 1964)
(35)	$O(^1D)+O_3\rightarrow 2O_2$	$k_{35}=10^{-11}$ (FITZSIMMONS and BAIR, 1964)
(36)	$H+O(^3P)+M\rightarrow OH+M$	$k_{36}=8\times10^{-33}$ (BATES and NICOLET, 1950)

Reactions 1 and 27—36 are unimportant for the present problem, but have been listed in order to show that they have been considered. Data for evaluation of dissociation rates have been summarized by HESSTVEDT (1968). The values used in this paper are given in Table 1, together with air temperatures and total number densities.

3. Photochemical model for the ozone layer. Computations are made for one latitude only. 15 degrees, summer, was selected because horizontal transport and organized vertical air motion is probably less important here than at higher latitudes.

On the basis of the reactions listed above, daytime photochemical equilibrium values of the number densities may be computed. Starting from these values, a first approximation of the night-time number densities may be computed. On the basis of such a crude model one obtains good estimates of the relative importance of the different reactions and of the characteristic times for the various components.

As always below 100 km, $O(^1D)$ has a very short characteristic time (less than 10^{-7} seconds). Photochemical equilibrium may therefore be assumed. Neglecting small terms we obtain

$$O(^1D)=\frac{J_{3b}\cdot O_3}{k_{20}\cdot M} \tag{3.1}$$

for daytime conditions. (In this paper the number density of $O(^1D)$ will be denoted by $O(^1D)$; similarly for the other components.) During the night $O(^1D)$ may be neglected.

Table 1. *Temperatures, air number densities and dissociation rates (in s^{-1})*

Height (km)	$T(°K)$	$M(cm^{-3})$	J_2	J_{3a}	J_{3b}	$J_{H_2O_2}=J_{HO_2}$	J_{H_2O}
40	254	8.6×10^{16}	5.1×10^{-10}	7.2×10^{-4}	1.6×10^{-3}	3.7×10^{-5}	1.8×10^{-10}
35	243	1.8×10^{17}	2.2×10^{-10}	7.2×10^{-4}	6.2×10^{-4}	1.9×10^{-5}	7.5×10^{-11}
30	232	3.8×10^{17}	5.7×10^{-11}	7.1×10^{-4}	2.4×10^{-4}	8.9×10^{-6}	1.8×10^{-11}
25	221	8.4×10^{17}	6.5×10^{-12}	6.9×10^{-4}	9.0×10^{-5}	4.7×10^{-6}	2.4×10^{-12}
20	207	2.0×10^{18}	4.2×10^{-13}	6.8×10^{-4}	5.0×10^{-5}	3.6×10^{-6}	1.6×10^{-13}
15	199	4.8×10^{18}	7.7×10^{-15}	6.7×10^{-4}	4.2×10^{-5}	3.3×10^{-6}	1.9×10^{-15}

Also the other atomic oxygen component, $O(^3P)$, has a very short characteristic time (less than 1 second) and photochemical equilibrium may be assumed. When small terms are neglected, the number density of $O(^3P)$ is computed from

$$O(^3P)=\frac{J_3\cdot O_3}{k_2\cdot M\cdot O_2} \tag{3.2}$$

for daytime conditions and from

$$O(^3P)_n=\frac{k_{15}\cdot OH_n^2}{k_2\cdot M\cdot O_2} \tag{3.3}$$

for night-time conditions. (Whenever there is a difference between daytime and night-time number densities, the latter are noted by subscript "n".)

Also atomic hydrogen has a very short characteristic time (less than 5×10^{-3} seconds) and photochemical equilibrium may be assumed. During the day we have

$$H = \frac{k_6 \cdot OH \cdot O(^3P) + J_{H_2O} \cdot H_2O}{k_8 \cdot M \cdot O_2 + k_9 \cdot O_3} \tag{3.4}$$

and during the night we have

$$H_n = \frac{k_6 \cdot O(^3P)_n + k_{19} \cdot H_2}{k_8 \cdot M \cdot O_2 + k_9 \cdot O_3} \cdot OH_n \tag{3.5}$$

where substitutions may be made for $O(^3P)$ and $O(^3P)_n$.

Also OH has a short characteristic time in the ozone layer: 3—4 seconds at 40 km increasing to 15 seconds at 15 km. Photochemical equilibrium may then be assumed and we have with a sufficient degree of accuracy.

$$OH = \frac{k_7 \cdot O(^3P) + k_{23} \cdot O_3}{k_6 \cdot O(^3P) + k_{24} \cdot O_3} \cdot HO_2 = \frac{k_7 \cdot J_3 + k_{23} \cdot k_2 \cdot M \cdot O_2}{k_6 \cdot J_3 + k_{24} \cdot k_2 \cdot M \cdot O_2} \cdot HO_2 \tag{3.6}$$

for daytime conditions and

$$OH_n = \frac{k_{23}}{k_{24}} \cdot HO_{2,n} \tag{3.7}$$

for night-time conditions.

Since the number densities of O(^{1}D), O(^{3}P), H and OH are given by their photochemical equilibrium values, substitution may be made in the equations for O_3, HO_2, H_2O_2, H_2O and H_2. When small terms are neglected in the equation for the ozone variation we obtain for daytime conditions

$$\frac{\partial O_3}{\partial t} = -2k_3 \cdot O(^3P) \cdot O_3 - (k_6 \cdot OH + k_7 \cdot HO_2) \cdot O(^3P) - (k_{23} \cdot HO_2 + k_{24} \cdot OH) \cdot O_3 + 2J_2 \cdot O_2 =$$

$$= -A \cdot O_3^2 - B \cdot HO_2 \cdot O_3 + C \tag{3.8}$$

where

$$A = \frac{2k_3 \cdot J_3}{k_2 \cdot M \cdot O_2}$$

$$B = 2\left(k_{23} + \frac{k_7 \cdot J_3}{k_2 \cdot M \cdot O_2}\right) \tag{3.9}$$

$$C = 2J_2 \cdot O_2$$

The night-time variation of ozone is very small, given by

$$\frac{\partial O_3}{\partial t} = -2k_{23} \cdot HO_{2,n} \cdot O_3 \tag{3.10}$$

The number density of ozone may then be computed from

$$A \cdot O_3^2 + \left(B + 2k_{23} \cdot \frac{HO_{2,n}}{HO_2} \cdot \frac{t_n}{t_d}\right) \cdot HO_2 \cdot O_3 - C = 0 \tag{3.11}$$

where t_d is the length of the day and t_n is the length of the night.

The characteristic time for HO_2 is of the order of an hour for daytime conditions; It is about 25 minutes at 40 km and increases to 4 hours at 15 km. For night-time conditions the characteristic time is about 20 hours. When substitution is made for the number densities of the short-lived components H and OH, the time variation of the number density of HO_2 is given by

$$\frac{\partial HO_2}{\partial t} = -2(k_{10} \cdot f + k_{13}) \cdot HO_2^2 + 2[(J_{H_2O_2} + k_{12} \cdot O(^3P)) \cdot H_2O_2 + k_{17} \cdot O(^1D) \cdot H_2O] \tag{3.12}$$

where $f = OH/HO_2$ is a constant, given by (3.6). With an accuracy which is sufficient for our purpose we may assume photochemical equilibrium:

$$HO_2^2 = \frac{[J_{H_2O_2} + k_{12} \cdot O(^3P)] \cdot H_2O_2 + k_{17} \cdot O(^1D) \cdot H_2O}{k_{10} \cdot f + k_{13}} \tag{3.13}$$

where the dissociation term is the largest term in the denominator and $k_{13} > k_{10} \cdot f$. The night-time variation is given by

$$\frac{\partial HO_{2,n}}{\partial t} = -2k_{10} \cdot \frac{k_{23}}{k_{24}} + k_{13} \cdot HO_{2,n}^2 \tag{3.14}$$

which gives

$$HO_{2,n} = \frac{HO_2}{1 + 2\left(k_{10} \cdot \frac{k_{23}}{k_{24}} + k_{13}\right) \cdot HO_2 \cdot t_n} \tag{3.15}$$

The time variation of the number density of H_2O_2 is given by

$$\frac{\partial H_2O_2}{\partial t} \approx -(J_{H_2O_2} + k_{12} \cdot O(^3P) + k_{14} \cdot OH) \cdot H_2O_2 + k_{13} \cdot (HO_2)^2 \tag{3.16}$$

but if we assume HO_2 to be in photochemical equilibrium, substitution may be made from (3.13). This gives

$$\frac{\partial H_2O_2}{\partial t} = -\left(k_{14} \cdot OH + \frac{f \cdot k_{10}}{k_{13} + f \cdot k_{10}}(J_{H_2O_2} + k_{12} \cdot O(^3P))\right) \cdot H_2O_2 + \frac{k_{13}}{k_{13} + f \cdot k_{10}}(J_{H_2O} + k_{17} \cdot O(^1D)) \cdot H_2O \tag{3.17}$$

Table 2. *Number densities (daytime conditions) in an atmosphere model where transport processes are neglected*

Height	$O(^1D)$	$O(^3P)$	O_2	O_3	OH	HO_2	H_2	H_2O	H	H_2O_2	O_3 (observed)
40 km	2.3×10^{2}	1.5×10^{9}	1.8×10^{16}	4.7×10^{11}	1.4×10^{6}	2.2×10^{7}	1.1×10^{6}	6.9×10^{11}	7.8×10^{2}	1.9×10^{8}	4.8×10^{11}
35 km	1.3×10^{2}	5.6×10^{8}	3.8×10^{16}	1.5×10^{12}	6.3×10^{5}	2.4×10^{7}	7.3×10^{5}	1.3×10^{12}	3.3×10^{1}	9.1×10^{8}	1.3×10^{12}
30 km	5.0×10^{1}	1.7×10^{8}	8.0×10^{16}	3.1×10^{12}	4.1×10^{5}	1.9×10^{7}	2.3×10^{5}	2.3×10^{12}	1.5	1.5×10^{9}	2.9×10^{12}
25 km	9.9	3.1×10^{7}	1.8×10^{17}	3.7×10^{12}	2.3×10^{5}	1.1×10^{7}	2.1×10^{4}	4.2×10^{12}	3.3×10^{-2}	1.0×10^{9}	5.3×10^{12}
20 km	1.2	2.4×10^{6}	4.1×10^{17}	2.0×10^{12}	1.1×10^{5}	5.3×10^{6}	4.4×10^{2}	8.0×10^{12}	2.3×10^{-4}	3.6×10^{8}	2.2×10^{12}
15 km	3.4×10^{-2}	3.2×10^{4}	9.8×10^{17}	1.5×10^{11}	6.1×10^{4}	3.1×10^{6}	4.1	1.1×10^{14}	8.2×10^{-7}	1.5×10^{8}	3.5×10^{11}

Table 3. *Characteristic times (daytime conditions) in an atmosphere model where transport processes are neglected*

Height	$O(^1D)$	$O(^3P)$	O_3	OH	HO_2	H_2	H_2O	H	H_2O_2
40 km	3.0×10^{-7}	1.3	1.3×10^{4}	3.2	3.2×10^{3}	5.8×10^{7}	1.4×10^{5}	7.8×10^{-3}	1.1×10^{5}
35 km	1.5×10^{-7}	2.9×10^{-1}	4.6×10^{4}	1.3	3.3×10^{3}	2.3×10^{8}	5.5×10^{5}	1.9×10^{-3}	4.2×10^{5}
30 km	6.9×10^{-8}	5.8×10^{-2}	1.9×10^{5}	6.4×10^{-1}	4.0×10^{3}	9.9×10^{8}	1.3×10^{6}	4.3×10^{-4}	1.1×10^{6}
25 km	3.1×10^{-8}	1.1×10^{-2}	1.1×10^{6}	5.5×10^{-1}	6.8×10^{3}	6.1×10^{9}	2.6×10^{6}	9.1×10^{-5}	2.4×10^{6}
20 km	1.3×10^{-8}	1.7×10^{-3}	5.8×10^{6}	1.0	1.4×10^{4}	5.2×10^{10}	3.8×10^{6}	1.6×10^{-5}	3.8×10^{6}
15 km	5.6×10^{-9}	2.9×10^{-4}	1.1×10^{7}	1.3×10^{1}	2.3×10^{4}	3.1×10^{11}	4.3×10^{6}	2.9×10^{-6}	4.3×10^{6}

Since the number densities of OH, $O(^3P)$ and $O(^1D)$ decrease considerably during the night, the night-time variation is negligible. The number density of H_2O_2 is therefore with a sufficient degree of accuracy given by

$$H_2O_2=\frac{k_{13}\cdot(J_{H_2O}+k_{17}\cdot O(^1D))}{(k_{13}+f\cdot k_{10})\cdot k_{14}\cdot OH+f\cdot k_{10}\cdot(J_{H_2O_2}+k_{12}\cdot O(^3P))}\cdot H_2O \tag{3.18}$$

H_2 has a very long characteristic time, so long that a model where transport processes are neglected cannot be expected to give realistic values for the number density of this component. However, in this model, we have

$$H_2=\frac{(k_{18}\cdot HO_2+k_{25}\cdot H_2O_2)\cdot H}{k_{21}\cdot O(^1D)+k_{22}\cdot O(^3P)+k_{19}\cdot OH} \tag{3.19}$$

The number density of water vapor is, in the present paper, taken as a constant at a given level. The mixing ratio is chosen in agreement with measurements, varying from 4×10^{-6} (by volume) at 15—20 km to 8×10^{-6} at 40 km.

The results of the computations are given in Tables 2, 3, 4, and 5. Observed values for ozone (HERING, 1964) are given for comparison. The agreement between theory and observation is striking. The level of maximum ozone is well predicted by the model, but the predicted peak number density is somewhat smaller than that found by observation.

Table 4. *Number densities (night-time conditions) for components having a diurnal variation. Transport processes are neglected. The number density of $O(^1D)$ is negligible throughout*

Height	$O(^3P)$	OH	HO_2	H
40 km	1.6×10^{-2}	6.5×10^{4}	3.3×10^{6}	4.5×10^{-7}
35 km	3.5×10^{-3}	6.6×10^{4}	3.3×10^{6}	4.4×10^{-8}
30 km	6.7×10^{-4}	6.4×10^{4}	3.2×10^{6}	1.8×10^{-9}
25 km	1.0×10^{-4}	5.8×10^{4}	2.9×10^{6}	1.7×10^{-11}
20 km	9.5×10^{-6}	4.5×10^{4}	2.2×10^{6}	1.9×10^{-14}
15 km	9.5×10^{-7}	3.4×10^{4}	1.7×10^{6}	2.4×10^{-17}

Table 5. *Characteristic times (night-time conditions) in an atmosphere model where transport processes are neglected ($O(^1D)$, $O(^3P)$ and H have the same characteristic times day and night)*

Height	O_3	OH	HO_2	H_2	H_2O	H_2O_2
40 km	1.5×10^{7}	4.3	1.5×10^{4}	1.8×10^{10}	3.8×10^{7}	3.8×10^{7}
35 km	1.5×10^{7}	1.4	1.3×10^{4}	3.1×10^{10}	3.8×10^{7}	3.8×10^{7}
30 km	1.6×10^{7}	6.4×10^{-1}	1.6×10^{4}	5.6×10^{10}	3.9×10^{7}	3.9×10^{7}
25 km	1.7×10^{7}	5.5×10^{-1}	2.7×10^{4}	1.2×10^{11}	4.3×10^{7}	4.3×10^{7}
20 km	2.2×10^{7}	1.0	5.9×10^{4}	3.9×10^{11}	5.6×10^{7}	5.6×10^{7}
15 km	2.9×10^{7}	1.3×10^{1}	1.0×10^{5}	6.3×10^{11}	7.3×10^{7}	7.3×10^{7}

4. Diffusion model for the ozone layer. A study of the characteristic times given in Tables 3 and 5 makes it clear that transport processes must play an important role for the vertical distribution of some of the components. This is especially obvious for H_2, which has a characteristic time of more than 10^{11} seconds at 15 km, increasing downwards. Unless other photochemical processes, disregarded in the present model, should decompose H_2 much more efficiently than reactions 19, 21, and 22, it must be concluded that H_2 is transported upwards from the ground to the tropopause without being broken down. The mixing ratio at the ground is, according to measurements by GLÜCKAUF and KITT (1957), 6×10^{-7}. This value will be taken as boundary condition at 15 km in our diffusion model. At the upper boundary we will assume photochemical equilibrium.

For ozone we shall assume observed values for the number density (HERING, 1964) in the troposphere (up to 17 km) and photochemical equilibrium at 40 km.

The third component which is likely to be influenced by eddy motion is H_2O_2. For this component we shall assume photochemical equilibrium as boundary conditions at 15 km and 40 km.

For the coefficient of vertical eddy diffusion K_z a value of 4×10^3 cm^2/s is assumed (PRABHAKARA, 1963) A steady state model is then computed using an iterative method. The region 15—40 km is divided into intervals of 1 km. When finite differences are introduced, the equation determining the number density of ozone at a given point takes the form

$$R_{O_3} \cdot O_3^2 + Q_{O_3} \cdot O_3 - P_{O_3} + Q^* \cdot O_3 - P^*_{O_3} = 0 \tag{4.1}$$

where

$$R_{O_3} = \frac{2k_3 \cdot J_3}{k_2 \cdot M \cdot O_2} \cdot \frac{t_d}{t_d + t_n} \tag{4.2}$$

$$Q_{O_3} = 2 \frac{\left(k_{23}(HO_2 \cdot t_d + HO_{2,n} \cdot t_n) + \dfrac{k_7 \cdot J_3 \cdot t_d}{k_2 \cdot M \cdot O_2} \right)}{(t_d + t_n)} \tag{4.3}$$

$$P_{O_3} = 2J_2 \cdot O_2 \cdot \frac{t_d}{t_d + t_n} \tag{4.4}$$

$$Q^* = \frac{2K_z}{(\Delta z)^2} \tag{4.5}$$

$$P^*_{O_3} = \frac{K_z}{(\Delta z)^2} \left[M \cdot \left(\frac{O_3'}{M'} + \frac{O_3''}{M''} \right) + \frac{(M' - M'')}{4} \left(\frac{O_3'}{M'} - \frac{O_3''}{M''} \right) \right] \tag{4.6}$$

One stroke (′) refers to the point above and two strokes (″) refer to the point below the point for which the computation is made.

The number density of H_2 is computed from

$$(Q_{H_2}+Q^*)\cdot H_2-P^*_{H_2}=0 \tag{4.7}$$

where

$$Q_{H_2}=\frac{(k_{21}\cdot O(^1D)+k_{22}\cdot O(^3P))t_d+k_{19}\cdot(OH\cdot t_d+OH_n\cdot t_n)}{t_d+t_n} \tag{4.8}$$

and

$$P^*_{H_2}=\frac{K_z}{(\Delta z)^2}\left[M\cdot\left(\frac{H_2'}{M'}+\frac{H_2''}{M''}\right)+\frac{(M'-M'')}{4}\left(\frac{H_2'}{M'}-\frac{H_2''}{M''}\right)\right] \tag{4.9}$$

The number density of H_2O_2 is computed from

$$Q_{H_2O_2}\cdot H_2O_2-P_{H_2O_2}+Q^*\cdot H_2O_2-P^*_{H_2O_2}=0 \tag{4.10}$$

where

$$Q_{H_2O_2}=\frac{k_{14}(OH\cdot t_d+OH_n\cdot t_n)+k_{10}\cdot f\cdot(J_{H_2O_2}+k_{12}\cdot O(^3P))\cdot t_d}{t_d+t_n} \tag{4.11}$$

$$P_{H_2O_2}=\frac{k_{13}\cdot t_d[(J_{H_2O}+k_{17}\cdot O(^3P))\cdot H_2O+(k_{21}\cdot O(^1D)+k_{22}\cdot O(^3P))\cdot H_2]}{(k_{13}+f\cdot k_{10})\cdot(t_d+t_n)} \tag{4.12}$$

$$P^*_{H_2O_2}=\frac{K_z}{(\Delta z)^2}\cdot\left[M\left(\frac{H_2O_2'}{M'}+\frac{H_2O_2''}{M''}\right)+\frac{(M'-M'')}{4}\left(\frac{H_2O_2'}{M'}-\frac{H_2O_2''}{M''}\right)\right] \tag{4.13}$$

It turns out, however, that the expressions (4.10) to (4.13) are inconvenient for numerical computations. A much faster convergence is obtained when substitutions are made for OH in (4.11). A comparison of the magnitude of the terms in (4.11) shows that the term $k_{17}\cdot O(^1D)\cdot H_2O$ is larger than the others by a factor of ten or more. This means that the number density of H_2O_2 is nearly proportional to the number density of water vapor. (3.13) may then be written

$$HO_2^2=\frac{J_{H_2O_2}+k_{12}\cdot O(^3P)+k_{17}\cdot O(^1D)\cdot H_2O/H_2O_2}{f\cdot k_{10}+k_{13}}\cdot H_2O_2=F\cdot H_2O_2 \tag{4.14}$$

where F, for practical purposes, may be regarded as a constant. Instead of (4.10) we then obtain upon substitution

$$R'_{H_2O_2}\cdot H_2O_2^{3/2}+Q'_{H_2O_2}\cdot H_2O_2-P'_{H_2O_2}+Q^*\cdot H_2O_2-P^*_{H_2O_2}=0 \tag{4.15}$$

where

$$R'_{H_2O_2}=k_{14}\cdot f\cdot F\cdot\frac{t_d}{t_d+t_n} \tag{4.16}$$

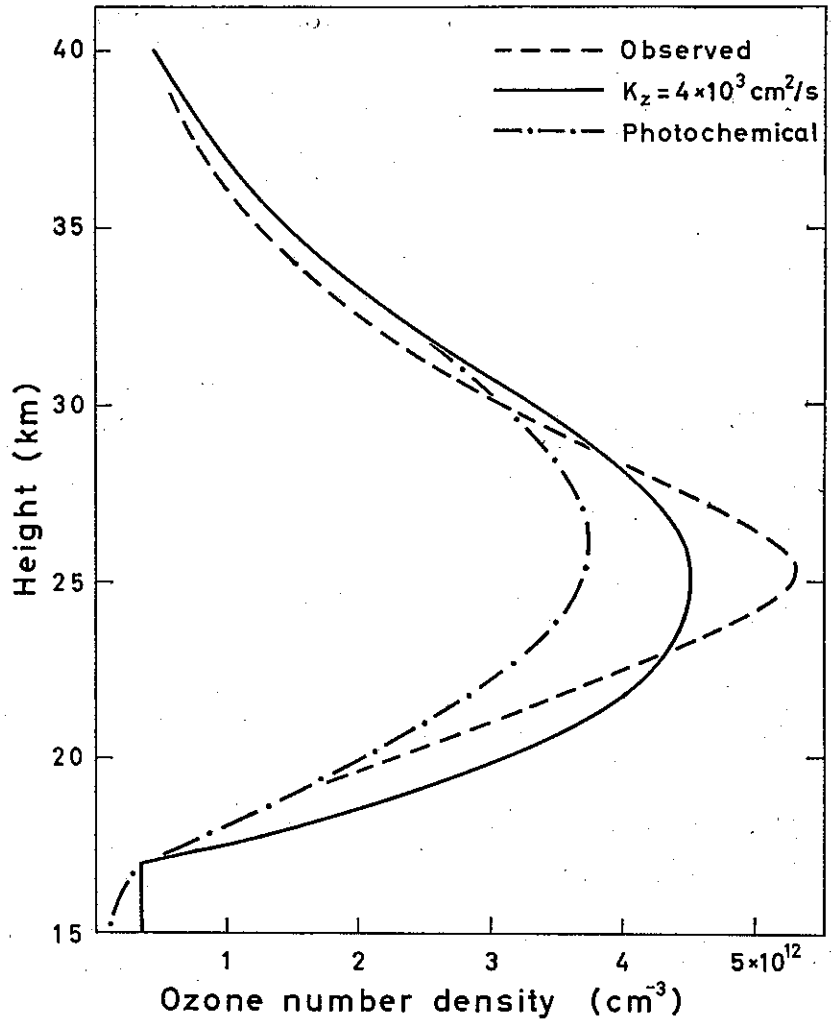

Figure 1. Vertical profiles of ozone, low latitudes. (- - - - - - observed values, - · - · - · - photochemical model without diffusion, ———— photochemical model with vertical eddy diffusion.)

$$Q'_{H_2O_2}=\left(\frac{f\cdot k_{10}}{k_{13}+f\cdot k_{10}}\cdot(J_{H_2O_2}+k_{12}\cdot O(^3P))+\frac{k_{14}\cdot k_{23}\cdot t_n}{k_{24}\cdot t_d}\cdot HO_{2,n}\right)\cdot\frac{t_d}{t_d+t_n} \tag{4.17}$$

$$P'_{H_2O_2}=\left(J_{H_2O}+\frac{k_{13}}{k_{13}+f\cdot k_{10}}\cdot k_{17}\cdot O(^1D)\right)\cdot H_2O.\frac{t_d}{t_d+t_n}$$

$$+[k_{21}\cdot O(^1D)+k_{22}\cdot O(^3P)]H_2\cdot\frac{t_d}{t_d+t_n}+k_{13}\cdot HO^2_{2,n}\cdot\frac{t_n}{t_d+t_n} \tag{4.18}$$

The number densities of the rest of the components, $O(^1D)$, $O(^3P)$, OH, HO_2 and H are computed from the expressions given in section 3, while fixed values are, as before, used for O_2 and water vapor. The results of the computations are shown in Tables 6—9 and in Figures 1—3.

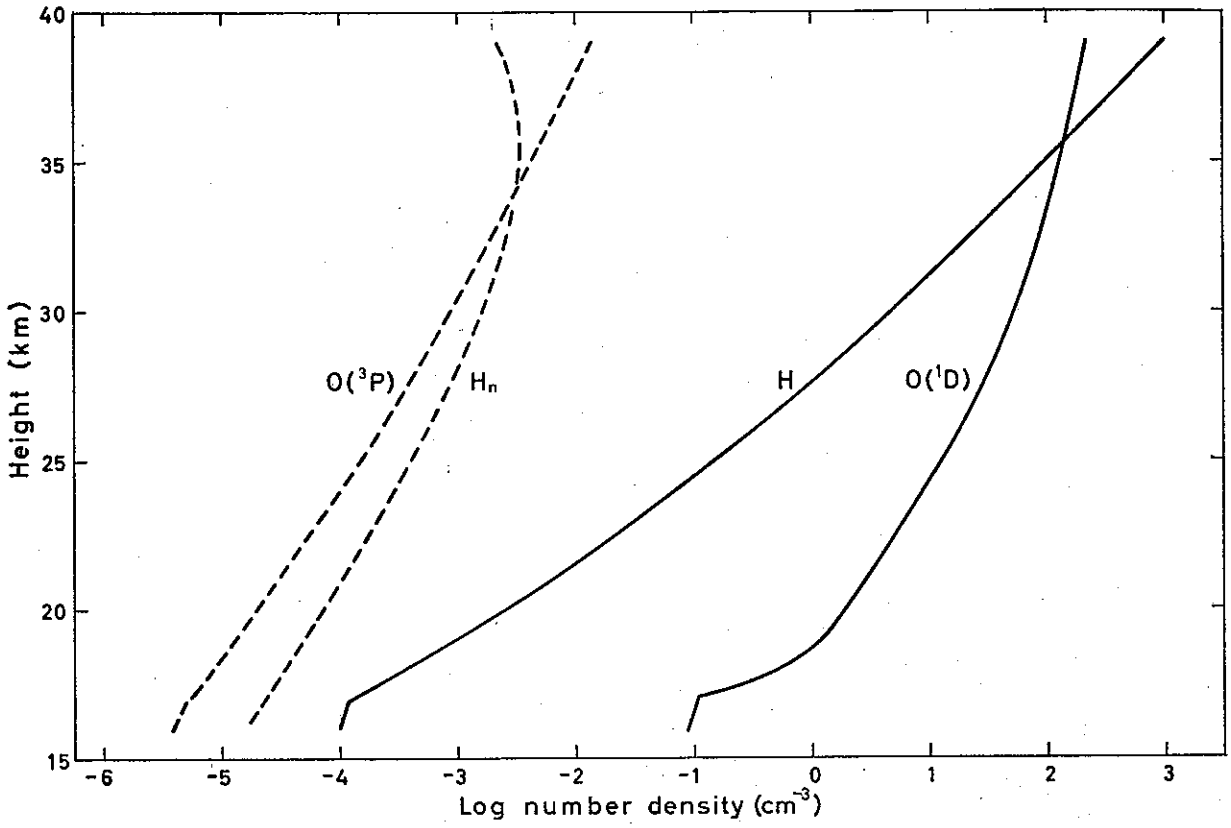

Figure 2. Computed number densities of oxygen-hydrogen components in the lower stratosphere. (When diurnal variations occur, night-time values are denoted by subscript "n".)

5. Discussion. It has already been mentioned that the effect of vertical eddy transport is most marked for molecular hydrogen. It turns out that H_2 is a major hydrogen component at all heights considered in this model. For $K_z = 4 \times 10^3$ cm^2/s, used in the present calculations, the number density mixing ratio decreases from 6×10^{-7} (boundary condition) at 15 km to 5.3×10^{-7} at 25 km and 7.3×10^{-8} at 35 km. These figures do not depend critically upon the value chosen for K_z. A computation was also made for $K_z = 4 \times 10^2$ cm^2/s, and mixing ratios of 4.4×10^{-7} (at 25 km) and 1.2×10^{-7} (at 35 km) were obtained.

The effect of vertical eddy transport on H_2O_2 and O_3 is less pronounced but still important since, for ozone, a higher degree of accuracy is required. In comparison with observed values the diffusion model must be considered as an improvement of the photochemical model.

Since the results depend on the choice we make for the parameters (dissociation rates, recombination rates and vertical eddy diffusion coefficient) it is of great interest to evaluate to what extent the result will depend on the choice of value for each parameter.

Above about 32 km, the first degree term in (3.8) is smaller than the second degree

Table 6. *Number densities (daytime conditions) in a photochemical atmosphere model with vertical eddy diffusion*

Height	$O(^1D)$	$O(^3P)$	O_2	O_3	OH	HO_2	H_2	H_2O	H	H_2O_2	O_3 (observed)
39 km	2.1×10^{2}	1.2×10^{9}	2.1×10^{16}	5.9×10^{11}	2.9×10^{6}	5.5×10^{7}	7.0×10^{9}	7.8×10^{11}	1.0×10^{3}	2.6×10^{8}	5.9×10^{11}
35 km	1.3×10^{2}	5.6×10^{8}	3.8×10^{16}	1.5×10^{12}	2.0×10^{6}	7.2×10^{7}	5.0×10^{10}	1.3×10^{12}	1.0×10^{2}	7.8×10^{8}	1.3×10^{12}
30 km	5.3×10^{1}	1.8×10^{8}	8.0×10^{16}	3.3×10^{12}	1.3×10^{6}	6.1×10^{7}	1.7×10^{11}	2.3×10^{12}	5.1	1.2×10^{9}	2.9×10^{12}
25 km	1.2×10^{1}	3.9×10^{7}	1.8×10^{17}	4.5×10^{12}	8.0×10^{5}	3.9×10^{7}	4.5×10^{11}	4.2×10^{12}	1.5×10^{-1}	9.6×10^{8}	5.3×10^{12}
20 km	2.2	4.3×10^{6}	4.1×10^{17}	3.5×10^{12}	5.2×10^{5}	2.6×10^{7}	1.1×10^{12}	8.6×10^{12}	2.9×10^{-3}	5.5×10^{8}	2.2×10^{12}
16 km	9.3×10^{-2}	8.9×10^{4}	8.6×10^{17}	3.5×10^{11}	3.3×10^{5}	1.6×10^{7}	2.4×10^{12}	3.7×10^{13}	1.0×10^{-4}	2.4×10^{8}	3.5×10^{11}

Table 7. *Characteristic times (daytime conditions) in a photochemical atmosphere model with vertical eddy diffusion*

Height	$O(^1D)$	$O(^3P)$	O_3	OH	HO_2	H_2	H_2O	H	H_2O_2
39 km	2.6×10^{-7}	9.8×10^{-1}	7.1×10^{4}	2.8	1.4×10^{3}	6.9×10^{7}	2.2×10^{5}	5.9×10^{-3}	1.7×10^{5}
35 km	1.5×10^{-7}	2.9×10^{-1}	2.0×10^{5}	1.4	1.0×10^{3}	2.0×10^{8}	4.1×10^{5}	1.9×10^{-3}	3.4×10^{5}
30 km	6.9×10^{-8}	5.8×10^{-2}	6.1×10^{5}	6.2×10^{-1}	1.3×10^{3}	7.7×10^{8}	9.0×10^{5}	4.3×10^{-4}	7.7×10^{5}
25 km	3.1×10^{-8}	1.1×10^{-2}	1.2×10^{6}	4.8×10^{-1}	1.9×10^{3}	3.7×10^{9}	1.6×10^{6}	9.1×10^{-5}	1.5×10^{6}
20 km	1.3×10^{-8}	1.7×10^{-3}	1.9×10^{6}	7.4×10^{-1}	3.0×10^{3}	2.1×10^{10}	2.3×10^{6}	1.6×10^{-5}	2.3×10^{6}
16 km	6.4×10^{-9}	3.6×10^{-4}	2.7×10^{7}	5.7	4.5×10^{3}	8.8×10^{10}	2.8×10^{6}	3.8×10^{-6}	2.8×10^{6}

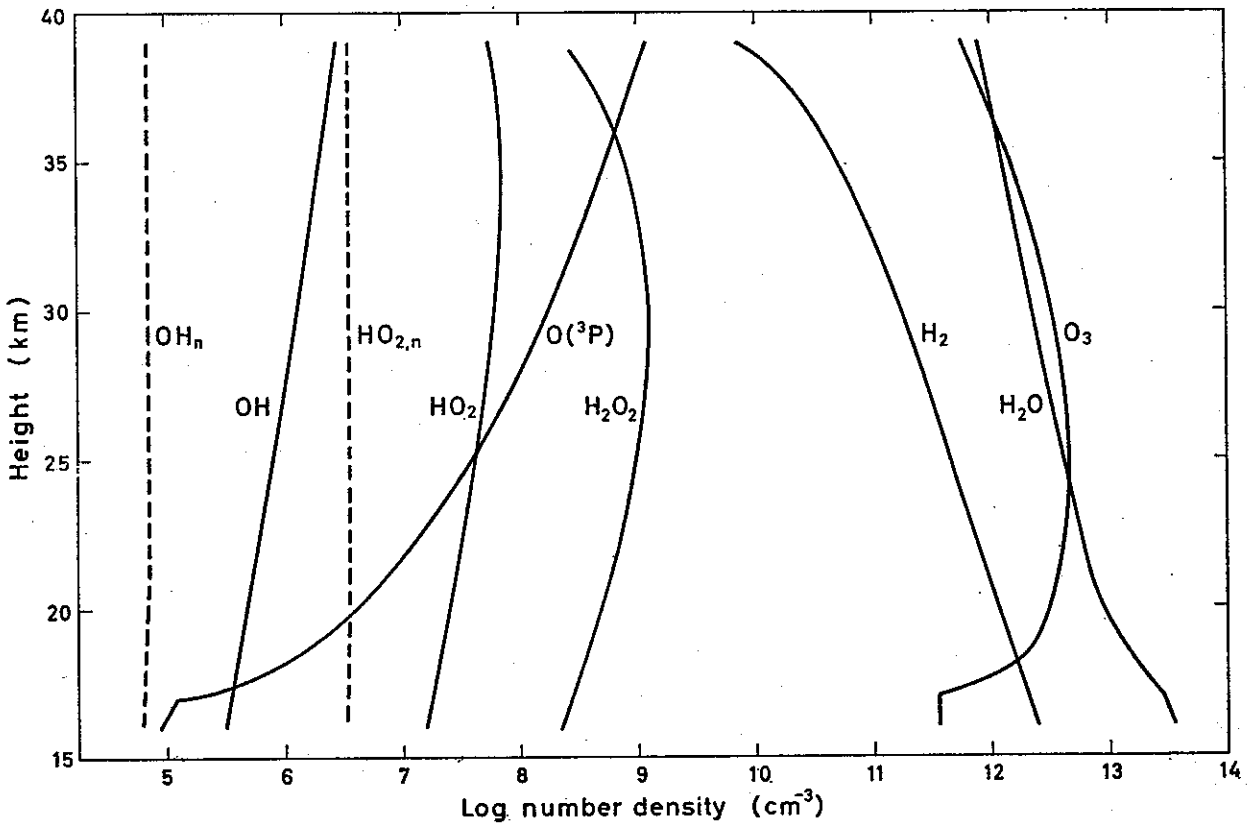

Figure 3. Computed number densities of oxygen-hydrogen components in the lower stratosphere. (When diurnal variations occur, night-time values are denoted by subscript "n". The night-time number density of $O(^1D)$ is negligible.)

term and the constant term. This means that the influence of hydrogen is relatively unimportant and that we have

$$O_3 \approx O_2 \cdot \sqrt{\frac{J_2 \cdot k_2 \cdot M}{J_3 \cdot k_3}} \tag{5.1}$$

Thus, above about 32 km, the dependence of the computed ozone number density on the choice of parameter values is easy to overlook.

Below about 32 km the picture becomes more complex and the importance of each reaction is often difficult to evaluate from analytic expressions. But the computations may be repeated for other choices of parameter values. This has been done and the results are given in Table 10. For each case a "skill-score" is computed by dividing the computed ozone number density by the observed value. The results of the computations corresponding to the parameter values selected in this paper are given in the first column, which should be used as a reference column.

It is of interest to note that the ozone profile is only to a small extent sensitive to the choice of value for the vertical eddy diffusion coefficient. It has already been

Table 8. *Number densities (night-time conditions) for components having a diurnal variation. Photochemical atmosphere model with vertical eddy diffusion. The number densities of $O(^1D)$ are negligible throughout*

Height	$O(^3P)$	OH	HO_2	H
39 km	1.4×10^{-2}	7.2×10^{4}	3.6×10^{6}	2.3×10^{-3}
35 km	4.4×10^{-3}	7.3×10^{4}	3.7×10^{6}	3.5×10^{-3}
30 km	8.7×10^{-4}	7.3×10^{4}	3.6×10^{6}	1.5×10^{-3}
25 km	1.5×10^{-4}	7.0×10^{4}	3.5×10^{6}	4.3×10^{-4}
20 km	2.1×10^{-5}	6.7×10^{4}	3.4×10^{6}	7.0×10^{-5}
16 km	4.0×10^{-6}	6.3×10^{4}	3.2×10^{6}	1.7×10^{-5}

Table 9. *Characteristic times (night-time conditions) in a photochemical atmosphere model with vertical eddy diffusion ($O(^1D)$, $O(^3P)$, and H have the same characteristic times day and night.)*

Height	O_3	OH	HO_2	H_2	H_2O	H_2O_2
39 km	1.4×10^{7}	3.4	5.6×10^{3}	1.8×10^{10}	3.5×10^{7}	3.5×10^{7}
35 km	1.4×10^{7}	1.4	4.3×10^{3}	2.8×10^{10}	3.4×10^{7}	3.4×10^{7}
30 km	1.4×10^{7}	6.3×10^{-1}	5.0×10^{3}	5.0×10^{10}	3.4×10^{7}	3.4×10^{7}
25 km	1.4×10^{7}	4.8×10^{-1}	7.8×10^{3}	9.6×10^{10}	3.6×10^{7}	3.6×10^{7}
20 km	1.5×10^{7}	7.4×10^{-1}	1.2×10^{4}	2.6×10^{11}	3.7×10^{7}	3.7×10^{7}
16 km	1.6×10^{7}	5.7	1.7×10^{4}	5.6×10^{11}	3.9×10^{7}	3.9×10^{7}

mentioned that also the H_2 and H_2O_2 profiles are only slightly dependent on the value of K_z. Standard profiles for H_2 and H_2O_2 may therefore be used without introducing too great errors in the ozone computations. This is of importance, for instance, for stratospheric circulation models where ozone computations are involved. The number density of HO_2 then becomes a constant at a given point, and the time variation of ozone density, due to photochemical reactions, is given by a simple differential equation.

It was mentioned above that the pure oxygen atmosphere model is a good approximation down to 32 km. Even down to 25 km the difference between the complete model and the pure oxygen model is relatively small. However, below the ozone maximum the influence of hydrogen is of vital importance. In this region the pure oxygen atmosphere model is misleading and should never be used in atmospheric circulation models.

Nevertheless, the parameters occurring in the pure oxygen atmosphere model are of extreme importance also for the oxygen-hydrogen model. It is therefore still of primary interest for theoretical ozone computations to have representative values of k_2, k_3, J_2, and J_3. The good results obtained in the present calculation do not necessarily mean that we know these quantities with a sufficient degree of accuracy; since it is the ratio $(J_2 \cdot k_2)/(J_3 \cdot k_3)$ which is important, the agreement between computation and observation may very well be due to a lucky combination of errors. Continued laboratory work on the basic oxygen reactions $O+O_2+M\rightarrow O_3+M$ and $O+O_3\rightarrow 2O_2$ is therefore of great interest.

Table 10. *"Skill-score", as defined in the text, for models with parameter values higher (') and lower (") than the values used in the present paper*

	Present model	$K_z''=K_z/10$	$k_3''=5.6\times10^{-11}\exp(-5700/RT)$	$J_2'=J_2\times5$	$J_3''=J_3/5$	$k_2'=k_2\times5$	$J_2''=J_2/5$
39 km	1.01	1.01	3.09	2.29	2.22	2.25	0.45
35 km	1.16	1.16	4.03	2.65	2.59	2.63	0.50
30 km	1.09	1.10	4.30	2.42	2.33	2.35	0.46
25 km	0.85	0.87	2.88	2.04	1.71	1.71	0.34
20 km	1.41	1.61	3.26	4.14	2.33	2.28	0.50
18 km	1.47	1.74	2.93	4.23	2.22	2.16	0.63

	$J_3'=J_3\times5$	$k_2''=k_2/5$	pure oxygen model	$k_{13}'=k_{13}\times10$	$k_{13}''=k_{13}/10$	$k_{23}'=k_{23}\times10$	$k_{23}''=k_{23}/10$	$k_7'=k_7\times10$
39 km	0.44	0.45	1.06	1.03	0.99	0.94	1.02	0.91
35 km	0.51	0.51	1.22	1.19	1.14	1.10	1.17	1.04
30 km	0.47	0.47	1.11	1.12	1.02	0.97	1.07	0.97
25 km	0.40	0.40	0.94	0.93	0.66	0.60	0.92	0.80
20 km	0.84	0.85	2.21	1.87	0.72	0.55	1.86	1.36
18 km	1.00	1.02	2.43	1.98	0.77	0.60	1.97	1.44

	$k_7'=k_7\times10$	$k_{10}'=k_{10}\times10$	$k_{10}''=k_{10}/10$	$k_{12}'=k_{12}\times10$	$k_{12}=k_{12}/10$	$k_{14}'=k_{14}\times10$	$k_{17}'=k_{17}\times10$	$k_{17}''=k_{17}/10$
39 km	1.03	1.04	0.97	1.01	1.01	1.02	0.93	1.03
35 km	1.18	1.19	1.14	1.16	1.16	1.18	1.09	1.19
30 km	1.11	1.11	1.08	1.06	1.06	1.07	1.05	1.08
25 km	0.86	0.89	0.85	0.86	0.87	0.87	0.93	1.03
20 km	1.44	1.62	1.40	1.44	1.44	1.48	1.38	1.47
18 km	1.50	1.70	1.46	1.50	1.49	1.18	1.44	1.54

	$k_{20}'=k_{20}\times10$	$k_{20}''=k_{20}/10$	$k_{21}'=k_{21}\times10$	$k_{22}'=k_{22}\times10$	$J_{H_2O_2}'=J_{H_2O_2}\cdot10$	$J_{H_2O_2}''=J_{H_2O_2}/10$	$\gamma'=\gamma\times10$	$\beta'=\beta\times5$
39 km	1.03	0.93	1.01	1.00	1.00	1.02	1.00	0.96
35 km	1.19	1.09	1.16	1.15	1.15	1.18	1.15	1.13
30 km	1.08	1.05	1.06	1.06	1.05	1.07	1.05	1.04
25 km	0.87	0.83	0.85	0.85	0.85	0.87	0.85	0.84
20 km	1.47	1.38	1.42	1.43	1.42	1.47	1.42	1.40
18 km	1.55	1.44	1.48	1.49	1.40	1.54	1.48	1.46

Variations in the parameters concerning hydrogen reactions turn out to have much smaller influence on the results than variations in the pure oxygen parameters. It is seen that two reactions are more important than the rest, namely reaction (13): $HO_2+HO_2 \rightarrow H_2O_2+O_2$ and reaction (23): $HO_2+O_3 \rightarrow OH+2O_2$. A precise knowledge of the reaction rates k_{13} and k_{23} seems to be of importance for ozone computations below 25 km. Other reactions are also important but not to the same extent.

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