Determination of parameters appearing in the "dry" and the "wet" photochemical theories for ozone in the stratosphere

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ABSTRACT

Existing photochemical theories of the ozone in the stratosphere have been investigated. It is indicated in this work that the ozone concentrations above 30 km between 0° and 45° latitude during the summer months are mainly determined by photochemical processes.

Parameters appearing in the schemes proposed by Chapman and Hampson are determined by fitting them to the mean ozone observations obtained from the Umkehr method. The results obtained simply that it is unlikely that any of the above mentioned theories alone can explain the ozone distributions. Numerical conditions on critical parameters are given. An alternative theory involving water vapour dissociation by excited molecular oxygen $O_2(^3\Sigma_u^+)$ is also discussed.

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1. Introduction

Recently measured rate constants for the reaction between atomic oxygen and ozone are so small that the ozone concentrations arising from applying the classical ("dry") photochemical theory for ozone (Chapman, 1930) are very different from the observations in the stratosphere (Hunt, 1966). It is therefore important to consider additional reactions. Bates & Nicolet (1950) point out the importance of hydrogen-oxygen compounds (H_2O, H, OH, O_2H) for the photochemistry of the mesosphere ("wet" theory). McGrath & Norrish (1960) give laboratory evidence that OH-radicals can be produced by a reaction between water vapor and excited atomic oxygen $O(^1D)$, a product of the ozone photodissociation in the Hartley band. In 1966, therefore, Hampson states that OH and O_2H might be present in high enough concentrations to play an important role even in the stratospheric ozone photochemistry.

In this paper we investigate if it is possible to explain the ozone observations between 30 and 35 km with the Hampson theory. It is indicated that at these levels the atmospheric ozone concentrations between 0° and 45° latitudes during summer is mainly determined by photochemical processes. It is therefore dubious to interpret all deviations between theory and observations in terms of atmospheric motions only. Our conclusions are that the Hampson theory is probably not adequate to explain the ozone observations between 30 and 35 km. This is the region of the atmosphere, where most of

[1] Contribution No. 105.

the atmospheric ozone is produced, although conditions are not very far from photochemical equilibrium.

2. The reaction scheme

The following reaction scheme for below 50 km, describing both the classical and the Hampson theory, may with very good accuracy be extracted from the scheme used by Hunt (1966).

(2.1) $O_2 + h\nu \xrightarrow{J_2} O + O$, $\lambda < 2425$ Å, see text

(2.2) $O_3 + h\nu \xrightarrow{J_3^*} O_2 + O^*$, $\lambda < 3080$ Å, see text

(2.3) $O_3 + h\nu \xrightarrow{J_3} O_2 + O$, 3080 Å $< \lambda <$ 11400 Å, see text

(2.4) $H_2O_2 + h\nu \xrightarrow{J_4} 2OH$, $\lambda < 5650$ Å, see text

(2.5) $O^* + M \xrightarrow{k_5} O + M$, $k_5 = 8 \times 10^{-11}$ (Schiff, 1968 and De More & Raper, 1964)

(2.6) $O + O_2 + M \xrightarrow{k_6} O_3 + M$, see text

(2.7) $O + O_3 \xrightarrow{k_7} 2\,O_2$, see text

(2.8) $O^* + H_2O \xrightarrow{k_8} 2OH$, see text

(2.9) $O_3 + OH \xrightarrow{k_9} O_2 + O_2H$, see text

(2.10) $O_3 + O_2H \xrightarrow{k_{10}} 2O_2 + OH$, see text

(2.11) $O + OH \xrightarrow{k_{11}} O_2 + H$, $k_{11} = 2 \times 10^{-11}$ (Schofield, 1967)

(2.12) $O_3 + H \xrightarrow{k_{12}} O_2 + OH$, $k_{12} = 2.6 \times 10^{-11}$ (Schofield, 1967)

(2.13) $O + O_2H \xrightarrow{k_{13}} O_2 + OH$, $k_{13} \geqslant 10^{-11}$ (Schofield, 1967)

(2.14) $H + O_2 + M \xrightarrow{k_{14}} O_2H + M$, $k_{14} = 4 \times 10^{-32}$ (Schofield, 1967)

(2.15) $OH + OH \xrightarrow{k_{15}} H_2O + O$, $k_{15} = 1.4 \times 10^{-11} \times \exp(-500/T)$ (Schofield, 1967)

(2.16) $OH + O_2H \xrightarrow{k_{16}} H_2O + O_2$, $k_{16} = 10^{-11}$ (Schofield, 1967)

(2.17) $O_2H + O_2H \xrightarrow{k_{17}} H_2O_2 + O_2$, $k_{17} = 3 \times 10^{-12}$ (Schofield, 1967)

(2.18) $OH + H_2O_2 \xrightarrow{k_{18}} O_2H + H_2O$, see text

During photochemical equilibrium conditions the production of odd oxygen by reaction (2.1) must be balanced by an equivalent removal in other reactions. In the classical theory by Chapman (1930) the balancing reaction in the stratosphere is (2.7). As a complement to this theory Hampson (1963) postulates production of OH via reactions (2.2) and (2.8) and subsequent destruction of odd oxygen particles by the reactions (2.9)–(2.13). Many of the rate coefficients appearing in this extended scheme are either poorly known or unknown. The problem is therefore very complex and the customary process of fitting the unknown parameters to ozone observations is a difficult task.

We will proceed by first simplifying the reaction scheme (choosing the unknown coefficients within certain limits), so that a simple ozone equation can be derived and then extrapolating the results from the simplified scheme. The question of the quantum yield of reaction (2.2) is also discussed.

We will now discuss the photochemical scheme in some detail.

Reactions (2.1–2.3)

All radiation with wavelengths shorter than 2424 Å has enough energy to dissociate molecular oxygen. Since the aim of this study is the photochemistry of ozone in the stratosphere, not all of these wavelengths need be considered, because within a large part of this wavelength-range the solar radiation is absorbed by the overlying atmosphere. With regard to dissociation of molecular oxygen we are justified in including merely the wavelength range from about 1900 to 2424 Å. With the same reasoning we can thus also safely disregard photodissociation of molecular oxygen and the associated production of $O(^1D)$ atoms by radiation with wavelengths less than 1750 Å.

The dissociation rate J_2 caused by direct solar radiation for reaction (2.1) is given by the integral

$$J_2 = \int_{\lambda < 2424\,\text{Å}} \alpha_{2\lambda}\, \tau_\lambda\, I_\lambda^{(o)}\, d\lambda \qquad (2.20)$$

where λ = wavelength of the radiation;

$\alpha_{2\lambda}$ = the absorption cross section of molecular oxygen at the wavelength λ;

$I_\lambda^o\, d\lambda$ = the solar flux in the wavelength region $(\lambda, \lambda + d\lambda)$ outside the atmosphere of the earth;

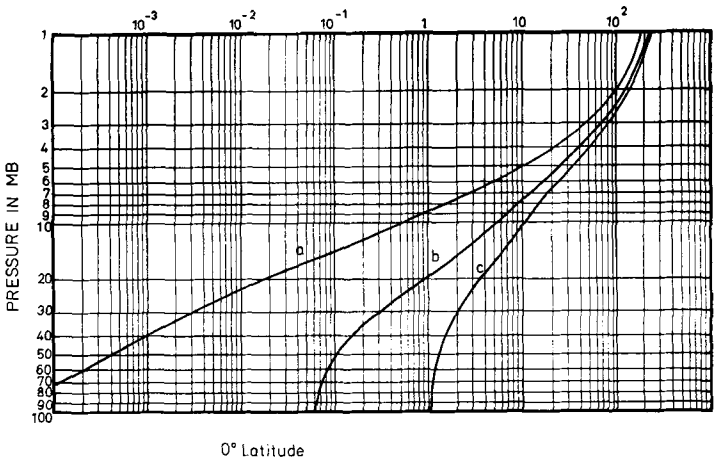


Fig. 1. $\int_0^{t_0} J_3^* dt$ as a function of the D-limit. a: 2880 Å, b: 2980 Å, c: 3080 Å. 0° latitude. $t_0 = 1$ day.

τ_λ = the monochromatic transmission for solar radiation at the wavelength λ.

Following Volman (1963) the quantum efficiencies are equated to unity.

During the entire study the assumption has been made that the atmosphere consists of plane, parallel, horizontally homogeneous layers. The effect of refraction has been neglected. Non-Rayleigh scattering as well as extinction of the beam of sunlight by atmospheric gases other than O_2, N_2 and O_3 has been disregarded. Thus the assumption has been made that the concentrations of other gases and aerosols in the middle and upper stratosphere are too low for them to play any important role in the redistribution or absorption of solar radiation. We thus write the transmission in the following way:

$$\tau_\lambda = \exp\left\{ -\frac{1}{\cos\theta}\left(\int_z^\infty \times (\alpha_{2\lambda}[O_2] + \alpha_{5\lambda}[M] + \alpha_{3\lambda}[O_3])\,dz'\right)\right\}. \quad (2.21)$$

where θ = the solar zenith angle,

$\alpha_{3\lambda}$ = the absorption cross section of ozone at the wavelength λ,

$\alpha_{5\lambda}$ = the Rayleigh coefficient for molecular scattering at the wavelength λ.

z, z' denote the vertical coordinate and $[O_2]$, $[O_3]$ and $[M]$ denote the concentrations of molecular oxygen, ozone and third bodies. A similar way of writing the concentrations will be applied for for all reactants in this paper.

The effect of Rayleigh scattering on the photochemistry of ozone, although included in this study, has been found to be of negligible importance in those atmospheric regions where photochemical processes are dominating, i.e. above 25 km.[1]

Within the wavelength region 1900 to 2425 Å two different sets of values of $I_\lambda^{(o)}$, $\alpha_{2\lambda}$ and $\alpha_{3\lambda}$ are obtainable. In this work initially the values recommended by Brewer & Wilson (1965) have been applied. Their data for $\alpha_{3\lambda}$ are the laboratory data given by Watanabe *et al.* (1958) and by Vigroux (1953). The $\alpha_{2\lambda}$ and $I_\lambda^{(o)}$ values tabulated by Brewer & Wilson imply "corrections" to the solar flux data given by Detwiler *et al.* (1961) and to the oxygen absorption coefficients given by Ditchburn & Young (1962). Around 2100 Å the Brewer–Wilson data on $\alpha_{2\lambda}$ are the values given by Ditchburn & Young multiplied by 0.75 and their data on $I_\lambda^{(o)}$ are those of Detwiler *et al.* multiplied by 0.36. The consequences arising from the use of the Detwiler *et al.* and the Ditchburn–Young data are also discussed.

There is little difference in the calculated J_2 between 25 and 40 km regardless of whether one uses Ditchburn–Young's or Brewer–Wilson's data for the absorption coefficient of molecular oxygen (Fig. 2).

[1] This will be discussed in more detail in a short paper which will appear in Tellus.

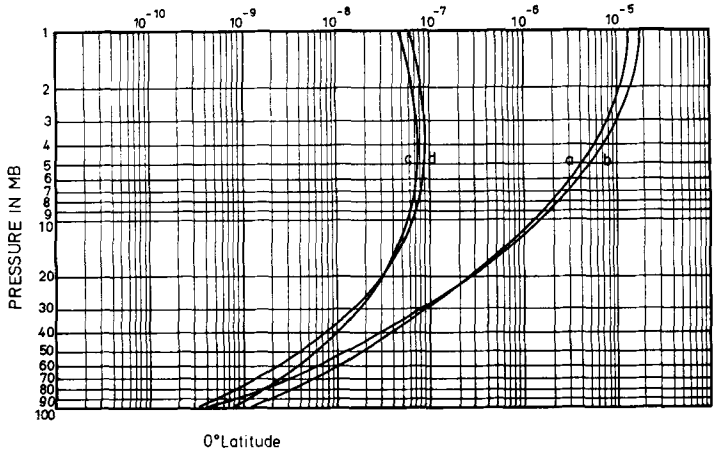


Fig. 2. $\int_0^{t_0} J_2 dt$ for direct (a, b) and (Rayleigh) scattered radiation (c, d); solar flux data from Brewer–Wilson (1965). a, c: Oxygen absorption coefficients from Brewer–Wilson (1965). b, d: Oxygen absorption coefficients from Ditchburn–Young (1962).

Below 40 km J_2 is mainly a function of solar radiation between 2000 and 2200 Å. The difference in the solar flux data according to Brewer–Wilson (1965) and Detwiler *et al.* (1961) implies that the J_2 values calculated from solar flux data by Brewer–Wilson (1965) are approximately 0.36 times the J_2 values calculated from the data by Detwiler *et al.* (1961). Therefore, the factor 0.36 only enters as a multiplicative one into this study.

According to Volman (1963), the following wavelength regions and dissociation products need to be considered with regard to reactions (2.2) and (2.3):

$$O_3(^1A) + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P); \quad \lambda < 11{,}400 \text{ Å} \tag{2.22a}$$

$$O_3(^1A) + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D); \quad \lambda < 3080 \text{ Å} \tag{2.22b}$$

$$O_3(^1A) + h\nu \rightarrow O_2(^1\Sigma_g^+) + O(^1D); \quad \lambda < 2660 \text{ Å} \tag{2.22c}$$

Here, the $O_3(^1A)$ state denotes the electronic ground state of the ozone, $O_2(^3\Sigma_g^-)$ the ground state and $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ excited states of molecular oxygen.

Although the second of the above processes is energetically possible for wavelengths less than approximately 3080 Å, there is a question on the quantum yield for $O(^1D)$ atoms, especially near this wavelength. For wavelengths larger than 3080 Å the products of the ozone dissociation are probably largely molecular oxygen and atomic oxygen in their ground states, because formation of other energetically possible products is spin forbidden. For radiation with wavelengths less than 3080 Å it is not at all evident that every light quantum absorbed by the ozone will actually produce an $O(^1D)$ atom. In order to be able to deal with this difficulty we will express the dissociation rates J_3^* and J_3 for reactions (2.2) and (2.3) by the following formulas:

$$J_3^* = \int_0^{3080-\Delta\lambda} \alpha_{3\lambda}\tau_\lambda I_\lambda^{(o)} d\lambda \tag{2.23a}$$

$$J_3 = \int_{3080-\Delta\lambda}^{11{,}400} \alpha_{3\lambda}\tau_\lambda I_\lambda^{(o)} d\lambda \tag{2.23b}$$

letting $\Delta\lambda$ assume different values.

Values for the ozone absorption cross sections corresponding to typical stratospheric temperatures for wavelengths above 2425 Å have been extracted from Vigroux (1953). Solar flux data are those given by Johnson (1954).

The way in which J_3 and J_3^* are formulated in (2.23a) and (2.23b) means that the quantum yield for the production of $O(^1D)$ atoms by reaction (2.2) will be taken equal to unity for wavelengths less than $(3080 - \Delta\lambda)$ Å and equal

to zero for radiation of larger wavelengths. However, these larger wavelengths will produce $O(^3P)$ with quantum efficiency equal to unity. De More and Raper (1962) have carried through laboratory experiments that indicate that the quantum yield for $O(^1D)$ formation is approximately 1 at 3000 Å, but decreases to 0.4 at 3100 Å. Because their laboratory experiments were performed under conditions very far from those prevailing in the stratosphere, their findings may not be applicable in the present case. One of the aims of this study will therefore be to examine more precisely the consequences of various choices of the quantum efficiency for $O(^1D)$ formation by reaction (2.2), including De More and Raper's. The value $(3080 - \Delta\lambda)$ Å will in the following discussion be called the D-limit. In this study the quantity $\Delta\lambda$ has been given values between 0 and 350 Å. Even if the above assumptions about the behaviour of the wavelength dependence of the quantum efficiency for reaction (2.2) is not quite correct, it will appear to be a suitable parameter to use in the discussion of the results obtained with the model that is developed.

The question of the quantum efficiency is of great importance for the photochemistry of the ozone in the stratosphere, because it influences very strongly the concentration of $O(^1D)$ atoms below 40 km, which in its turn determines the concentration of OH and O_2H and thus the importance of the catalytic reactions (2.9)–(2.13). This comes from the fact that the absorption cross section of ozone decreases rapidly from very high values at the center of the Hartley band to much lower values around 3100 Å. The transmission of the atmosphere in this band is therefore a rapidly varying function of the wavelength for given total amounts of ozone. This is illustrated by Fig. 1. The D-limit is thus an important parameter in this study, because of its influence on the ozone profile and total amounts.

Reactions (2.4) and (2.18)

Depending on the magnitudes of J_4 and k_{18}, reaction (2.17) will or will not be an important loss process for OH– and O_2H-molecules. In appendix 1 we will prove that reaction (2.4) may be neglected if

$$k_{18} \geqslant 4 \times 10^{-13} \qquad (2.24)$$

(2.24) agrees with the conditions given by Foner & Hudson (1962).

Nicolet (1966) estimates

$$k_{18} = 1.5 \times 10^{-12} \sqrt{T}.$$

There is therefore reason to believe that relation (2.24) is fulfilled and accordingly reaction (2.4) will be neglected already from this point on.

Reactions (2.6) and (2.7)

There is a very large variety in results obtained in laboratories for the rate coefficients of these reactions, mainly with regard to their temperature dependence. This disagreement stems mainly from the derived activation energy for reaction (2.7) and gives for observed stratospheric temperatures k_7-values that deviate by more than one order of magnitude. For a broader discussion reference is made to the reviews by Schiff (1964, 1968).

It is important to mention here that laboratory experiments to determine these rate coefficients have shown to be very sensitive to catalytic destruction by trace substances, one of which is water vapour (Schiff, 1964).

With regard to the k_6 values we will initially assume that the data given by Clyne *et al.* (1965) are correct.

$$k_6 = 9 \times 10^{-36} \exp(1180/T). \qquad (2.25)$$

Consequences of other choices of k_6 will however also be discussed. It will become clear that knowledge of the single rate constant k_6 is of importance in the Hampson theory, while in the classical theory it is merely the ratio k_7/k_6 which is of great weight.

It is well known from the "classical" theory that very different ozone profiles will be obtained for different choices of the ratio k_7/k_6. It might therefore be worth while to deduce reasonable values for this ratio from ozone observations.

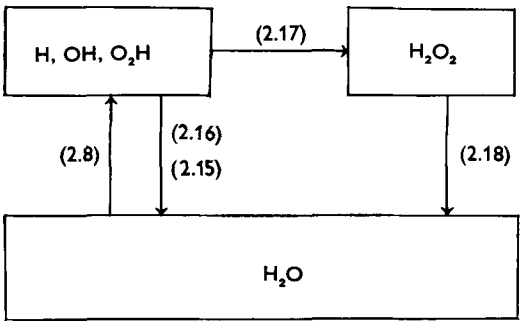
Reactions (2.8)–(2.18)

The rate coefficients for the reactions (2.8), (2.9) and (2.10) are unknown at present. Kaufman (1964) has shown that at room temperature $k_9 \leqslant 5 \times 10^{-13}$; k_{10} is probably much smaller. In this study we will initially assume that for the stratosphere

$$5 \times 10^{-15} \leqslant k_{10} < k_9 \leqslant 10^{-13};\ k_{13} = 10^{-11}. \quad (2.26)$$

This assumption will make it possible for us to deduce a relatively simple equation which describes the rate of change of ozone concentrations in the stratosphere. We will, however, also be able to deal with the situation, by means of an extrapolation, when the above assumption is not satisfied.

Let us conclude this section by illustrating the chemical exchange between the hydrogen compounds in our reaction scheme. We will (for reasons which will become clear in the next section) consider one combined box for the H-, OH- and O_2H-particles and further one each for the water vapour and the hydrogen peroxide. Exchanges between the boxes are given by arrows with the reaction numbers indicated.



Exchange inside the (H, OH and O_2H)-box occurs through the reactions (2.9)–(2.14), which do not change the total concentration of H-, OH- and O_2H-particles.

It should again be pointed out, that with our choice of rate coefficients, production of hydrogen peroxide by reaction (2.17) is not balanced by photo-dissociation of H_2O_2 (reaction (2.4)), but by reaction (2.18), above 30 km.

3. The photochemical equations

In section 3.1 we prove that the assumptions made about k_9–k_{13} allow us to disregard the reactions (11)–(13) in the lower regions of the stratosphere (below 35 km). In section 3.2 we derive the photochemical equations for each of the chemical constituents. The final aim is to derive an equation which gives the change of the ozone concentration over 24 hours. This equation forms the basis for further discussions.

3.1 Further reduction of the reaction scheme

OH, O_2H and H are in mutual chemical equilibrium through the reactions (2.9)–(2.13) if the outflow of particles from the (H, OH, O_2H)-box is appreciably slower than the conversion of these particles inside the box. Let us assume this, explore the consequences and finally verify that the results are consistent with our initial assumptions on the rate coefficients.

$$\{k_9[OH] + k_{10}[O_2H] + k_{12}[H]\}\,[O_3] + \{k_{11}[OH] + k_{13}[O_2H]\}\,[O] + k_{18}[OH]\,[H_2O_2] \geqslant 2\{k_{15}[OH]^2 + k_{16}[OH]\,[O_2H] + k_{17}[O_2H]^2\}. \quad (3.1)$$

Equilibrium for H_2O_2 and H yield:

$$k_{18}[OH]\,[H_2O_2] = k_{17}[O_2H]^2 \quad (3.2)$$

$$k_{11}[O]\,[OH] = k_{12}[O_3]\,[H] + k_{14}[H]\,[O_2]\,[M] \quad (3.3a)$$

Below 50 km $k_{14}[O_2]\,[M] \gg k_{12}[O_3]$, so that

$$k_{12}[O_3]\,[H] < k_{11}[O]\,[OH] \quad (3.3b)$$

By (3.3b) and (3.2) condition (3.1) therefore becomes

$$\{k_9[OH] + k_{10}[O_2H]\}\,[O_3] + \{k_{11}[OH] + k_{13}[O_2H]\}\,[O] \gg 2k_{15}[OH]^2 + 2k_{16}[OH]\,[O_2H] + k_{17}[O_2H]^2. \quad (3.4)$$

Condition (3.4), which gives equilibrium inside the box, implies that

$$\frac{[O_2H]}{[OH]} = \frac{k_9[O_3] + k_{11}[O]}{k_{10}[O_3] + k_{13}[O]}. \quad (3.5)$$

Already now using the approximate, well known expression (3.15) for $[O]/[O_3]$ we find from (2.26) that below 35 km with good accuracy

$$k_{11}[O] < k_9[O_3] \quad (3.6a)$$

$$k_{13}[O] < k_{10}[O_3] \quad (3.6b)$$

and therefore

$$k_9[OH] = k_{10}[O_2H]. \quad (3.7)$$

The exact height range over which this approximation is valid is dependent on the values of the constants k_8, k_9, k_{10}, k_{11} and k_{13}. The alternative

case, when the applied conditions are not fulfilled is therefore also discussed.

Equations (3.7) and (2.26) give

$$[O_2H] \gg [OH] \tag{3.8}$$

so that according to (3.6a), (3.6b) and (3.8) conditions (3.4), (3.1) become

$$\{k_9[OH] + k_{10}[O_2H]\}\,[O_3] \gg k_{17}[O_2H]^2. \tag{3.9}$$

In the "wet" theory photochemical balance between production and destruction of odd oxygen particles yields according to (3.7):

$$J_2[O_2] = k_9[OH]\,[O_3] = k_{10}[O_2H]\,[O_3] \tag{3.10a}$$

so that conditions (3.9), (3.1) finally become

$$2k_{10}^2[O_3]^2 \gg k_{17}\,J_2[O_2].$$

It is now easily verified that the right hand side in this expression is at most 15% of the left hand side, when J_2 is calculated with the Brewer-Wilson data and therefore (3.1) is a valid approximation.

We can approximately indicate the mean concentration for OH and O_2H between 30 and 35 km required by the assumptions that we have made. From (3.10a)

$$\frac{\bar{J}_2[O_2]}{k_9[O_3]} = \overline{[OH]} \tag{3.10b}$$

$$\frac{\bar{J}_2[O_2]}{k_{10}[O_3]} = \overline{[O_2H]} \tag{3.10c}$$

where the bar sign denotes mean concentrations over one day and consequently from (2.26)

$$\frac{\bar{J}_2[O_2]}{10^{-13}[O_3]} \leqslant \overline{[OH]} < \overline{[O_2H]} \leqslant \frac{\bar{J}_2[O_2]}{5\times 10^{-15}[O_3]} \tag{3.10d}$$

which yields at 35 km:

$$2\times 10^7 \leqslant \overline{[OH]} < \overline{[O_2H]} \leqslant 4\times 10^8 \tag{3.11a}$$

and at 30 km:

$$10^7 \leqslant \overline{[OH]} < \overline{[O_2H]} \leqslant 2\times 10^8 \tag{3.11b}$$

From now on we only consider the reactions (2.1)–(2.3), (2.5)–(2.10) and (2.15)–(2.18).

3.2. Derivation of photochemical equations

We now proceed by deducing the photochemical equations for the reactants in our reduced scheme.

O-equation*

With $k_5 = 8\times 10^{-11}$ the characteristic time of O* is much less than 1 sec and thus O* must always be very close to photochemical equilibrium. Therefore,

$$[O^*] = \frac{J_3^*[O_3]}{k_5[M]}. \tag{3.12}$$

O-equation

Again, we may safely assume that the atomic oxygen is very near to chemical equilibrium. Remembering (3.11a), (3.11b) and (3.12) we easily find:

$$[O] = \frac{2J_2[O_2] + J_{3t}[O_3]}{k_6[O_2][M] + k_7[O_3]} \tag{3.13}$$

where

$$J_{3t} = J_3 + J_3^*. \tag{3.14}$$

Because $J_2[O_2] \ll J_{3t}[O_3]$ and $k_7[O_3] \ll k_6[O_2]\,[M]$ below 50 km, we find that

$$[O] = \frac{J_{3t}[O_3]}{k_6[O_2][M]}. \tag{3.15}$$

OH, O_2H equations

Equation (3.7) may be rewritten in the following way

$$[OH] = \delta Y \tag{3.16a}$$

$$[O_2H] = (1-\delta)\,Y \tag{3.16b}$$

with

$$Y = [OH] + [O_2H] \tag{3.17}$$

and

$$\delta = \frac{k_{10}}{k_9 + k_{10}}. \tag{3.18}$$

We write the following equation for the time rate of change of Y:

$$\frac{\partial Y}{\partial t} = 2k_8[O^*][H_2O] - 2k_{15}[OH]^2 - 2k_{16}[OH] \times [O_2H] - 2k_{17}[O_2H]^2.$$

Inserting (3.16a), (3.16b) we find

$$\frac{\partial Y}{\partial t} = 2k_8[O^*][H_2O] - \beta Y^2 \tag{3.19}$$

with $\beta = 2\{\delta^2 k_{15} + \delta(1-\delta)k_{16} + (1-\delta)^2 k_{17}\}$. (3.20a)

Because of (2.26) we know that $0 < \delta < 1$ and therefore

$$\beta \approx 2k_{17} = 6 \times 10^{-12}. \qquad (3.20b)$$

Variations in β as a function of δ are very small. We will now prove that Y is almost in photochemical equilibrium. From (3.11a) and (3.11b) it follows that the mean value of Y over one day is much larger than 10^7.

Writing $Y = Y_e + \eta$, where Y_e is the photochemical equilibrium value of Y from equation (3.19) and where $|\eta| < Y_e$ we easily find from (3.19) that

$$\frac{\partial \eta}{\partial t} = -2\beta Y_e \eta.$$

The restoration time for Y, that is the time needed to reduce a deviation from photochemical equilibrium to $1/e$ of its initial value, is therefore equal to $1/(2\beta Y_e)$. Because $\beta = 6 \times 10^{-12}$ and Y_e (daytime) $\gg 10^7$, we find that the restoration time for Y-particles during daytime is much less than 2 hours and therefore short enough to assume photochemical equilibrium.

The night-time concentrations of Y can be neglected. This is shown in the following way.

At night, equation (3.19) simplifies to:

$$\frac{\partial Y}{\partial t} = -\beta Y^2.$$

From this equation the following relation can easily be derived

$$Y(t) = \frac{Y(o)}{1 + \beta Y(o) t} \qquad (3.21)$$

where $Y(o)$ is the value of Y at sunset and $Y(t)$ is the value of Y at time t after sunset.

We now find by integrating (3.21)

$$\int_0^{t_n} Y dt = \frac{1}{\beta}\{\ln (1 + Y(o)\beta t_n)\} \qquad (3.22)$$

where t_n = length of night.

Inserting $Y(o) \gg 10^7$

$\beta = 6 \times 10^{-12}$

$t_n = 12$ hours.

We finally find:

$$\frac{1}{t_n Y(o)} \int_0^{t_n} Y dt < 0.3. \qquad (3.23)$$

The concentrations of OH and O_2H during night-time may therefore safely be neglected. We have therefore proved that treating the OH and O_3H as being in photochemical equilibrium is a very good approximation.

For the same reason we can say that photochemical ozone variations during night-time certainly should not be expected in the altitude region treated here.

With Y in photochemical equilibrium it follows from (3.19) that

$$Y = \sqrt{\frac{2k_8[H_2O][O^*]}{\beta}}. \qquad (3.24)$$

Inserting the expression for $[O^*]$ from (3.12) we get

$$Y = \sqrt{\frac{2k_8[H_2O]}{\beta k_5[M]} J_3^*[O_3]}. \qquad (3.25)$$

Between 30 and 35 km, the relative variations from one day to another in the ozone concentrations are small (see Dütsch, 1966). We may therefore treat $[O_3]$ as being constant during one day. The same will also be assumed to be true for the water vapor concentration. Defining

$$t_0 = \text{one day} \qquad (3.26)$$

we obtain by integrating expression (3.25) over one day

$$\overline{Y} = \frac{1}{t_0} \int_0^{t_0} Y dt = \sqrt{\frac{2k_8[H_2O]}{\beta k_5[M]}} \sqrt{[O_3]} \overline{\sqrt{J_3^*}} \qquad (3.27)$$

$$\overline{\sqrt{J_3^*}} = \frac{1}{t_0} \int_0^{t_0} \sqrt{J_3^*}\, dt \qquad (3.28)$$

O_3 equation

Below 50 km $[O_3] \gg [O] + [O^*]$. Furthermore, because O and O* are in photochemical equilibrium with the prevailing ozone concentration, we can be sure that any change of odd oxygen particles in this altitude region essentially reflects a change in the ozone concentration. Denoting the concentration of odd oxygen particles

$$U = [O] + [O^*] + [O_3] \qquad (3.29]$$

the following relation can easily be derived:

$$\frac{\partial}{\partial t}[O_3] = \frac{\partial U}{\partial t} = 2J_2[O_2] - 2k_7[O][O_3] - \{k_9[OH] + k_{10}[O_2H]\}[O_3]. \quad (3.30)$$

We here insert the expression for [O] from (3.15) and take the mean over 24 hours. This yields

$$\frac{\partial}{\partial t}\overline{[O_3]} = 2\bar{J}_2[O_2] - \frac{2k_7\overline{[O_3]^2}\bar{J}_{3t}}{k_6[O_2][M]} - \overline{[O_3]}\{k_9\overline{[OH]} + k_{10}\overline{[O_2H]}\}. \quad (3.31)$$

In the above formulae

$$\bar{J}_2 = \frac{1}{t_0}\int_0^{t_0} J_2 dt \quad (3.32)$$

$$\bar{J}_{3t} = \frac{1}{t_0}\int_0^{t_0} J_{3t} dt \quad (3.33)$$

Combination of expressions (3.31), (3.16a), (3.16b) and (3.18) now readily yields

$$\frac{\partial}{\partial t}\overline{[O_3]} = 2\bar{J}_2[O_2] - \frac{2k_7\overline{[O_3]^2}\bar{J}_{3t}}{k_6[O_2][M]} - \frac{2k_9k_{10}}{k_9+k_{10}}\overline{[O_3]}\,\bar{Y}. \quad (3.34)$$

Next, inserting $\bar{Y}$ from (3.27), we obtain

$$\frac{\partial}{\partial t}\overline{[O_3]} = 2\bar{J}_2[O_2] - \frac{2k_7\overline{[O_3]^2}\bar{J}_{3t}}{k_6[O_2][M]} - \gamma\overline{\sqrt{J_3^*}}\,\overline{[O_3]}^{\frac{3}{2}} \quad (3.35)$$

where $\overline{[O_3]}$ = the mean ozone concentration over one day, and

$$\gamma = \frac{2k_9k_{10}}{k_9+k_{10}}\sqrt{\frac{\overline{2k_8[H_2O]}}{\beta\ k_5[M]}}. \quad (3.36)$$

With the aid of (2.26) and (3.20b) we may simplify, so that

$$\gamma = 1.2\times10^6 k_{10}\sqrt{\frac{\overline{k_8[H_2O]}}{k_5[M]}}. \quad (3.37)$$

We have now arrived at our basic equation (3.35), which gives the rate of change of mean ozone concentration over 24 hours. The right hand member of this expression contains one production term $2J_2[O_2]$ and two destruction terms. The first of the destruction terms describes the destruction of ozone under the conditions given by the classical "dry" ozone photochemistry, while the second describes the reduction of the ozone by catalytic destruction through OH- and O_2H-radicals. When photochemical processes are dominating, that is when $(\partial/\partial t)\overline{[O_3]} = 0$ in (3.35), there must exist a balance between the production term and the two destruction terms for odd oxygen. We will now assume that we need only consider one of the destruction terms. We thus regard only the two following possibilities:

(a) If the first destruction term is much larger than the second one equation (3.35) describes the "dry" photochemistry of ozone (Dütsch, 1946). From a given vertical ozone distribution the terms $\bar{J}_2$ and $\bar{J}_{3t}$ can be determined and consequently the factor k_7/k_6. In this way we may obtain this ratio from observations. In the case of the classical "dry" ozone photochemistry the derived balance equation should be correct between 30 and 50 km.

(b) If the second destruction term is much larger than the first one the destruction of atmospheric ozone in the lower part of the stratosphere occurs mainly by the catalytic reactions (9) and (10). Again, with known ozone distribution we can calculate $\sqrt{J_3^*}$, the magnitude of which is very dependent on the quantum yield of $O(^1D)$ atoms in the process (2.2). For different choices of the D-limit we obtain very different height dependences of $\sqrt{J_3^*}$ (see Fig. 1). The requirements of balance between the production $2\bar{J}_2[O_2]$ and the destruction term will give us γ as a function of altitude from equation (3.35).

From the behavior of γ as a function of altitude we can draw interesting conclusions regarding the photochemistry in the ozone-hydrogen atmosphere.

4. Influence of the atmospheric motions on the ozone distribution

In this section we will study part of the problem of the behaviour of the atmospheric ozone under the combined influence of photochemistry and atmospheric motions. Since we will consider the mean ozone concentration obtained from Umkehr measurements whenever the restoration time is less than 10 days as approximately

representing photochemical equilibrium concentrations, we have to justify this assumption. In part 4.1 of this section we will derive expressions for the restoration time for ozone under the conditions described by both the "dry" and the "wet" photochemistry. In part 4.2 we will compare the magnitudes of the two terms describing the rate of change of ozone concentration under the influence of photochemical and dynamical processes and justify our assumption.

4.1. *Restoration times for ozone*

Equation (3.35) can be approximated and written as

$$\frac{\partial x}{\partial t} = P - Ax^2 - Bx^{\frac{3}{2}} \tag{4.1}$$

with $A = \dfrac{2k_7\bar{J}_{3t}}{k_6[O_2][M]}$, $B = \gamma\sqrt{\bar{J}_3^*}$, $P = 2\bar{J}_2[O_2]$, $x = \overline{[O_3]}$.

In accordance with the foregoing discussion two special cases will be considered:

(a) $Ax^2 \gg Bx^{3/2}$ (classical theory)

(b) $Bx^{3/2} \gg Ax^2$ ("wet" photochemistry).

Let us call the equilibrium value of $\overline{[O_3]} = x_e$ and let us denote the deviation from photochemical equilibrium ξ, so that

$$x = x_e + \xi. \tag{4.2}$$

4.1.1. $Ax^2 \gg Bx^{3/2}$.

In this case we have:

$$x_e = \sqrt{\frac{P}{A}} = [O_2]\sqrt{\frac{k_6\bar{J}_2[M]}{k_7\bar{J}_{3t}}}. \tag{4.3}$$

Inserting x from (4.2) in (4.1) yields

$$\frac{\partial \xi}{\partial t} = P - A(x_e+\xi)^2 = -A\xi(2x_e+\xi).$$

From this expression one can determine the characteristic time of restoration τ_r for ozone, that is the time it takes to reduce a deviation from the photochemical equilibrium value to $1/e$. We find

$$\tau_r = \frac{1}{2Ax_e}\ln\left(\frac{\xi+2ex_e}{\xi+2x_e}\right) \tag{4.4a}$$

and therefore

$$\tau_r = \frac{e-1}{Ax}, \quad \text{if } x_e < \xi \text{ (lower stratosphere, troposphere)} \tag{4.4b}$$

and

$$\tau_r = \frac{1}{2Ax_e} = \frac{1}{4}\sqrt{\frac{k_6[M]}{k_7\bar{J}_{3t}\bar{J}_2}}, \quad \text{if } |\xi| \ll x_e \text{ (above 30 km).} \tag{4.4c}$$

Above 30 km we may therefore write

$$\frac{\partial \xi}{\partial t} = -\frac{\xi}{\tau_r}. \tag{4.5}$$

Because the ratio k_6/k_7 is not known with certainty, another expression than (4.4c) for the ozone restoration time above 30 km which is more practical for computational purposes can be derived in the following way. From (4.4c) and (4.1) it follows that

$$\tau_r = \frac{x_e}{4\bar{J}_2[O_2]}.$$

Approximating x_e by the actually observed mean ozone concentration it is thus possible to estimate τ_r without having an exact knowledge of k_6 and k_7. In doing so we probably do not make a large error above 30 km. Therefore:

$$\tau_r = \frac{[O_3]_{\text{observed}}}{4\bar{J}_2[O_2]}. \tag{4.6}$$

We also see that with regard to the magnitude of τ_r the same factor of difference ~ 0.36 between the solar flux data around 2100 Å according to Brewer-Wilson (1965) and to Detwiler *et al.* (1961) appears.

4.1.2 $Bx^{3/2} \gg Ax^2$

In this case:

$$x_e = \left(\frac{P}{B}\right)^{\frac{2}{3}} = \frac{2\bar{J}_2[O_2]^{\frac{2}{3}}}{\gamma\sqrt[3]{\bar{J}_3^*}}. \tag{4.7}$$

Inserting x from (4.2) in (4.1) yields

$$\frac{\partial \xi}{\partial t} = P - B(x_e+\xi)^{\frac{3}{2}} \tag{4.8}$$

and for the photochemical restoration times we find:

$$\tau_r = \frac{2}{B}\frac{e^{\frac{1}{2}}-1}{x^{\frac{1}{2}}}, \text{ if } x_e \ll \xi \text{ (troposphere, lower stratosphere)} \quad (4.9\,a)$$

$$\tau_r = \frac{2}{3Bx_e^{\frac{1}{2}}}, \text{ if } |\xi| \ll x_e \text{ (above 30 km)} \quad (4.9\,b)$$

Above 30 km, equation (4.8) reads

$$\frac{\partial \xi}{\partial t} = -\frac{\xi}{\tau_r}. \quad (4.10)$$

Also, in this case a more practical formula for τ_r than equation (4.9 b) may easily be derived.

$$\tau_r = \frac{x_e}{3\bar{J}_2[O_2]}$$

and therefore approximately:

$$\tau_r = \frac{[O_3]_{\text{observed}}}{3\bar{J}_2[O_2]}. \quad (4.11)$$

By comparing equations (4.6) and (4.11) we see that above 30 km the approximate restoration times for the "wet" photochemistry are slightly larger than those for the "dry" case. Depending on the value of the D-limit, for other parts of the stratosphere and for the troposphere the opposite might be true.

By inserting the expression for γ from (3.36) into (4.7) and (4.9 b) we can easily find that both the restoration time and the ozone equilibrium concentrations are proportional to $[H_2O]^{-\frac{1}{2}}$. An increase by a factor of 2 in the water vapour concentrations means thus a reduction by 25% in both the restoration time and the concentration of the ozone. Above 30 km, where the ozone restoration time is less than 10 days, there might exist a negative correlation between ozone and water vapour concentrations in the sense that high water vapour concentrations imply lower ozone concentrations. The water vapour concentration is not influenced greatly by the ozone.

4.2. Photochemistry and atmospheric motions

Under the influence of photochemical processes and atmospheric motions we arrive at the following equations for the time rate of change of the ozone mixing ratio:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial \phi}{\partial t}\right)_{ph} - v\frac{\partial \phi}{\partial y} - w\frac{\partial \phi}{\partial z}. \quad (4.13)$$

In this expression $\phi = [O_3]/[M]$, the particle mixing ratio of ozone, while y, z are coordinates in a local Cartesian system chosen positive in the north- and upward direction respectively, and v and w are the corresponding wind velocities. The first term on the right hand side $(\partial\phi/\partial t)_{ph}$ denotes the rate of production by photochemical processes. Any deviation from photochemical equilibrium must essentially come from meridional and vertical motions and therefore we have neglected the term describing zonal variations of ϕ in expression (4.13). For the moment, let us concentrate on the effect of an almost constant vertical motion of a time scale longer than one day. Then

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial \phi}{\partial t}\right)_{ph} - w\frac{\partial \phi}{\partial z}. \quad (4.14)$$

Taking the mean value of this equation over one day we obtain

$$\frac{\partial \bar{\phi}}{\partial t} = \frac{1}{[M]}\frac{\partial \xi}{\partial t} - w\frac{\partial \bar{\phi}}{\partial z} \quad (4.15)$$

where, as before, ξ denotes the deviation of $[O_3]$ from the photochemical equilibrium value.

Following (4.5) or (4.10), for small deviations from photochemical equilibrium we may write

$$\frac{1}{[M]}\frac{\partial \xi}{\partial t} = \frac{-\xi}{[O_3]}\frac{\bar{\phi}}{\tau_r}. \quad (4.16)$$

With regard to the vertical ozone profile near pressure level p_0 we can write

$$\bar{\phi}(p) = \bar{\phi}(p_0)\left(\frac{p}{p_0}\right)^a \quad (4.17)$$

where $\phi(p)$ denotes the ozone particle mixing ratio at a nearby pressure level p. Above about 27 km we estimate from the ozone Umkehr observations collected by Dütsch (1964) that $|a| \leq 0.25$. As has already been discussed, the variability of the profile generally is not large.

Making use of the hydrostatic approximation and relation (4.17) we find

$$w\frac{\partial\bar{\phi}}{\partial z} = \frac{-wa}{H}\bar{\phi} = \frac{-\bar{\phi}}{\tau_m} \tag{4.18}$$

where: H = scale height of the atmosphere (~ 6.5 km) (4.19)

and $$\tau_m = \frac{H}{wa}. \tag{4.20}$$

We may interpret the quantity $|\tau_m|$ as a characteristic time needed for deviations from photochemical equilibrium to occur by atmospheric motion.

Inserting (4.16) and (4.18) into (4.15) we arrive at

$$\frac{\partial\bar{\phi}}{\partial t} = -\bar{\phi}\left(\frac{\xi}{[O_3]}\frac{1}{\tau_r} - \frac{1}{\tau_m}\right) \tag{4.21}$$

We shall now compare the magnitudes of the terms

$$\frac{\xi}{[O_3]}\frac{1}{\tau_r} \text{ and } \frac{1}{\tau_m}.$$

Because of the difference between the radiation data from Brewer-Wilson and Detwiler *et al.* the numerical conditions we arrive at differ approximately by a factor 0.36 depending on which data are used. In the following all numerical values corresponding to the Detwiler *et al.* data are given in parentheses immediately following the values corresponding to the Brewer-Wilson data.

Let us consider conditions where the relative deviation of the ozone concentration from its photochemical equilibrium concentration is at least 20%. Further we assume that $\tau_r \leqslant 10$ days (4 days). Then, in order for the term describing the rate of change of ozone concentrations by atmospheric motions to be larger than the term describing the rate of change of ozone concentrations by photochemical processes, w has to be at least 6 mm/sec (15 mm/sec) at the levels considered.

Direct observations of vertical velocities are not available. However, the critical vertical velocity 6 mm/sec (15 mm/sec) seems to be very large in comparison to the velocities that one can reasonably infer from observations. According to Ebdon (see Murgatroyd, 1968), in the region between the equator and 45°, and between the 25 and 35 km levels, standard deviations of temperatures are at most 7°C. Some of this is probably due to observational errors. In the presence of vertical motions in excess of 6 mm/sec, adiabatic temperature changes of more than 6°C/day could be observed, since radiative processes at 30 km have time scales much larger than one day (Lindzen-Goody, 1965). It seems to be true therefore that vertical motions of time scales much larger than one day cannot cause the mean ozone profile to deviate more than 20% from the photochemically determined profile.

Since we may estimate from Dütsch (1964) that the characteristic length scale for ozone variations in the meridional direction between 0° N and 45° N is 2×10^3 times the characteristic length scale of variations in the vertical, a corresponding critical value for v is approximately 12 m/sec (30 m/sec). Mean meridional wind velocities and their standard deviations for winter and summer seasons at certain stations have been given by Newell (1965). From his data the conclusions may be drawn that between 25 and 35 km between equator and 45° N the meridional wind velocities are less than 6 m/sec during the summer months. From this fact we conclude that meridional motions with time scales larger than one day are usually too weak to cause larger than 20% deviation of the mean ozone profile from photochemical equilibrium, at least during the summer months. But of course the effect of eddy motions may be more important.

We deal with the eddy motions, also including motions with time scales shorter than one day, by applying the eddy diffusion theory, as described by Reed & German (1965). In this case the rate of change of ozone concentration, now neglecting the effect of mean motions, may be written as

$$\frac{\partial}{\partial t}\overline{\overline{[O_3]}} = \left(\frac{\partial}{\partial t}\overline{\overline{[O_3]}}\right)_{ph} + \frac{\partial}{\partial y}\left([M]K_{yy}\frac{\partial\bar{\bar{\phi}}}{\partial y} + [M]K_{yz}\frac{\partial\bar{\bar{\phi}}}{\partial z}\right) + \frac{\partial}{\partial z}\left([M]K_{yz}\frac{\partial\bar{\bar{\phi}}}{\partial z} + [M]K_{zz}\frac{\partial\bar{\bar{\phi}}}{\partial z}\right). \tag{4.22}$$

In (4.22) $\overline{\overline{[O_3]}}$ and $\bar{\bar{\phi}}$ denote time (seasonal) and zonal average values, while K_{yy}, K_{yz} and K_{zz} are the eddy diffusion coefficients.

Because we only want to make a rough determination of critical magnitudes of the eddy diffusion coefficients K_{yy}, K_{yz} and K_{zz}, we will now treat these parameters as constants. Drop-

ping the double bar signs, the above equation (4.20) therefore simplifies to

$$\frac{\partial}{\partial t}[O_3] = \left(\frac{\partial}{\partial t}[O_3]\right)_{ph} + K_{yy}[M]\frac{\partial^2\phi}{\partial y^2} + K_{yz}[M]\frac{\partial^2\phi}{\partial y \partial z} + K_{yz}\frac{\partial}{\partial z}\left([M]\frac{\partial\phi}{\partial y}\right) + K_{zz}\frac{\partial}{\partial z}\left([M]\frac{\partial\phi}{\partial z}\right). \quad (4.23)$$

Again, we will approximate $[O_3]$ and ϕ by the mean values given by the "Umkehr" observations. We write:

$$\frac{\partial\phi}{\partial y} \approx \delta\frac{\partial\phi}{\partial z} \quad (4.24)$$

where δ is the ratio of the characteristic length for ozone variations in the vertical and in the meridional direction. Between 0° and 45° and in the height region between 25 and 40 km we may estimate (Dütsch, 1964):

$$\delta \approx 5 \times 10^{-4}. \quad (4.25)$$

With the aid of (4.16), (4.17), (4.18) and (4.24) we can transform (4.23) into

$$\frac{1}{[O_3]}\frac{\partial[O_3]}{\partial t} = \frac{-\xi}{[O_3]}\frac{1}{\tau_r} + \delta^2 K_{yy}\frac{a^2}{H^2} + \delta K_{yz}\frac{a(2a+1)}{H^2} + K_{zz}\frac{a(a+1)}{H^2}. \quad (4.26)$$

Again, as before, taking $\xi/[O_3] \geqslant 0.2$, $|a| \approx 0.25$ and $H \approx 6.5$ km, those values of the eddy coefficients that make any one of the eddy exchange terms (4.24) equal in magnitude to that describing the rate of change by photochemical processes become equal to

$$K_{yy} = 3 \times 10^{12} \text{ cm}^2/\text{second}$$
$$K_{yz} = 5 \times 10^{8} \text{ cm}^2/\text{second}$$
$$K_{zz} = 2 \times 10^{5} \text{ cm}^2/\text{second}.$$

Any one of the above listed critical values is considerably much larger than those determined by Reed & German (1965) based on heat flux data for the 30 mb level. Most critical seems to be the value of K_{zz}. The maximum value derived by Reed & German for this quantity is 6×10^3 cm²/sec.

Although the above discussion is not claimed to be a strict proof, because of some simplifications applied in the study, it nevertheless strongly suggests that if $\tau_r < 10$ days, especially in the summer and autumn, the ozone distribution between the 0° and 45° latitudes is mainly under photochemical control with concentrations given by appropriate mean radiational conditions. The atmospheric motion is not strong enough to change the photochemically determined ozone profile to a large degree. This large effect of photochemical processes on the ozone distribution above 30 km and probably even lower in summer is strongly connected with the high static stability of the stratosphere.

It should be added that below the level of the maximum ozone concentration the effect of atmospheric motions on the determination of the mean ozone profile becomes very strong, because both τ_r and $|a|$ become quickly larger with decreasing altitude.

We must conclude that the ozone observations, at least in those regions where the ozone restoration time is less than 10 days, have to be explained by a photochemical theory. In view of the arguments given in this section it is very dubious to interpret large deviations between theory and observations in this region by the influence of atmospheric motions. The mean ozone "Umkehr" observations of course do not exactly reflect the photochemical equilibrium values. However, the conclusions we will draw regarding the photochemical theories are valid even when relative deviations from photochemical equilibrium are as great as 20%. This will become clear when we discuss the results.

5. Discussion of the results

We shall first discuss briefly, in section 5.1, the results with regard to the "classical" photochemical theory for the ozone in the stratosphere, including the reactions (2.1), ((2.2) + (2.3)), (2.6) and (2.7). In section 5.2 the Hampson theory, with reactions (2.9)–(2.13) replacing reaction (2.7), will be studied.

5.1. The classical theory

The following well known formula, derived from (3.35), applies for the ratio k_7/k_6:

$$\frac{k_7}{k_6} = \frac{\bar{J}_2[O_2]^2[M]}{\bar{J}_3[O_3]^2}. \quad (5.1)$$

Numerical values of this ratio for different seasons, latitudes and observed mean ozone distributions, have been calculated. It was found

Table 1. *The factor γ from equation (3.36), multiplied with 10^{10}. Radiation data according to Brewer & Wilson, and Johnson. D-limit at 2880 Å; at pressure levels to the left of the lines the time of restoration of ozone is less than 10 days*

Latitude	Season	Pressure in mb: 5	6	7	8	9	10	12	14	16	18	20
0°		*4.0*	*3.9*	*3.8*	*3.8*	*3.7*	*3.7*	*3.6*	3.7	3.8	3.8	4.0
30°	Spring	*4.1*	*4.1*	*4.0*	*3.9*	*3.9*	*3.9*	*3.9*	3.9	4.0	4.0	4.0
30°	Summer	*5.0*	*4.3*	*4.1*	*4.0*	*4.0*	*3.9*	*3.8*	3.9	4.0	4.0	4.2
30°	Autumn	*4.5*	*4.1*	*4.1*	*4.0*	*4.0*	*3.9*	3.9	4.1	4.2	4.2	4.1
30°	Winter	*5.7*	*5.0*	*5.0*	*4.6*	*4.5*	4.2	4.1	4.1	3.9	3.7	3.6
45°	Spring	*4.7*	*4.4*	*4.2*	*4.2*	*4.2*	4.2	4.2	4.2	4.2	4.1	3.7
45°	Summer	*4.7*	*4.3*	*4.2*	*4.2*	*4.2*	*4.2*	*4.2*	4.2	4.3	4.5	4.5
45°	Autumn	*5.4*	*5.2*	*5.0*	*4.6*	*4.5*	*4.5*	4.5	4.4	4.2	4.2	4.1
45°	Winter	*5.7*	*5.7*	*5.6*	5.2	5.0	4.8	4.2	3.8	3.4	3.0	2.6

that the calculated k_7/k_6 ratios between 30 and 50 km do not at all reflect the large temperature dependence given by laboratory investigations. The computed ratio, using the Brewer-Wilson (1965) data, is approximately 2.5×10^{19} and independent of temperature. Going through the list of measured ratios by Schiff (1964) we find only one set of data (Urbach *et al.*) which is of the right order of magnitude and has a low enough temperature dependence to be compatible with the classical theory. However, the reliability of the data has been seriously questioned by Schiff (1964). Other listed values are both too small and show too large a temperature dependence to provide satisfactory ozone profiles and total ozone amounts. This last point was also indicated by Hunt (1966) and Nicolet (1966). The situation is even less satisfactory when we use the solar flux data given by Detwiler *et al.* (1961).

We are therefore led to the conclusion that reactions other than reaction (2.7) must be to a large extent responsible for the destruction of odd oxygen particles above 30 km.

5.2. Ozone photochemistry including OH, O_2H reactions

In this theory it follows from (3.35) that

$$\gamma = \frac{2\bar{J}_2[O_2]}{\sqrt{J_3^*}[O_3]^{\frac{1}{2}}}, \tag{5.2}$$

where γ is defined by (3.36) or (3.37). It is possible to calculate values of γ for different observed ozone distributions and choices of the D-limit. Some results are shown in Tables 1–5. The discussion will now continue along the following alternatives:

Table 2. *The factor γ from equation (3.36), multiplied with 10^{10}. Radiation data according to Brewer & Wilson, and Johnson. D-limit at 2930 Å; at pressure levels to the left of the lines the time of restoration of ozone is less than 10 days*

Latitude	Season	Pressure in mb: 5	6	7	8	9	10	12	14	16	18	20
0°		*2.9*	*2.5*	*2.2*	*2.0*	*1.9*	*1.7*	*1.5*	1.4	1.3	1.4	1.4
30°	Spring	*2.9*	*2.7*	*2.3*	*2.0*	*1.9*	*1.7*	1.6	1.5	1.4	1.4	1.3
30°	Summer	*3.5*	*2.8*	*2.4*	*2.1*	*2.0*	*1.8*	*1.6*	1.5	1.4	1.4	1.4
30°	Autumn	*3.0*	*2.6*	*2.2*	*2.0*	*1.9*	*1.7*	1.6	1.5	1.4	1.4	1.3
30°	Winter	*3.7*	*3.0*	*2.6*	*2.3*	*2.0*	1.8	1.5	1.3	1.2	1.1	1.1
45°	Spring	*3.0*	*2.6*	*2.2*	*2.0*	*1.8*	1.7	1.5	1.4	1.3	1.2	1.2
45°	Summer	*3.2*	*2.7*	*2.3*	*2.2*	*2.0*	*1.9*	*1.7*	1.6	1.5	1.5	1.5
45°	Autumn	*3.5*	*3.0*	*2.7*	*2.3*	*2.0*	*1.9*	1.7	1.5	1.3	1.3	1.2
45°	Winter	*3.1*	*2.8*	*2.4*	2.1	1.8	1.6	1.3	1.1	1.0	0.8	0.7

Table 3. *The factor γ from equation (3.36), multiplied with 10^{10}. Radiation data according to Brewer & Wilson, and Johnson. D-limit at 2980 Å; at pressure levels to the left of the lines the time of restoration of ozone is less than 10 days*

Latitude	Season	Pressure in mb 5	6	7	8	9	10	12	14	16	18	20
0°		*2.3*	*1.8*	*1.5*	*1.3*	*1.2*	*1.0*	*0.8*	0.7	0.6	0.6	0.5
30°	Spring	*2.3*	*2.0*	*1.6*	*1.3*	*1.2*	*1.0*	0.8	0.7	0.6	0.6	0.5
30°	Summer	*2.8*	*2.2*	*1.7*	*1.4*	*1.3*	*1.2*	*0.9*	0.8	0.7	0.6	0.6
30°	Autumn	*2.3*	*1.8*	*1.5*	*1.3*	*1.1*	*1.0*	0.8	0.7	0.6	0.5	0.5
30°	Winter	*2.8*	*2.0*	*1.7*	*1.4*	*1.2*	1.0	0.7	0.6	0.5	0.4	0.4
45°	Spring	*2.2*	*1.8*	*1.4*	*1.2*	*1.0*	0.9	0.7	0.6	0.5	0.4	0.4
45°	Summer	*2.5*	*2.0*	*1.6*	*1.4*	*1.3*	*1.1*	*0.9*	0.8	0.7	0.6	0.6
45°	Autumn	*2.7*	*2.2*	*1.8*	*1.4*	*1.2*	*1.1*	0.8	0.7	0.6	0.5	0.4
45°	Winter	*2.1*	*1.8*	*1.4*	1.1	0.9	0.7	0.5	0.4	0.3	0.2	0.2

Table 4. *The factor γ from equation (3.36), multiplied with 10^{10}. Radiation data according to Brewer & Wilson, and Johnson. D-limit at 3030 Å; at pressure levels to the left of the lines the time of restoration of ozone is less than 10 days*

Latitude	Season	Pressure in mb 5	6	7	8	9	10	12	14	16	18	20
0°		*2.0*	*1.6*	*1.3*	*1.1*	*0.9*	*0.8*	*0.6*	0.5	0.4	0.3	0.3
30°	Spring	*2.0*	*1.7*	*1.3*	*1.1*	*0.9*	*0.8*	0.6	0.5	0.4	0.3	0.3
30°	Summer	*2.5*	*1.9*	*1.4*	*1.2*	*1.0*	*0.9*	*0.7*	0.5	0.4	0.4	0.3
30°	Autumn	*2.0*	*1.5*	*1.2*	*1.0*	*0.9*	*0.7*	0.6	0.5	0.4	0.3	0.3
30°	Winter	*2.3*	*1.7*	*1.4*	*1.1*	*0.9*	0.7	0.5	0.4	0.3	0.2	0.2
45°	Spring	*1.9*	*1.5*	*1.2*	*0.9*	*0.8*	0.7	0.5	0.4	0.3	0.2	0.2
45°	Summer	*2.2*	*1.7*	*1.4*	*1.1*	*1.0*	*0.8*	*0.7*	0.5	0.5	0.4	0.3
45°	Autumn	*2.3*	*1.8*	*1.4*	*1.1*	*0.9*	*0.8*	0.6	0.4	0.3	0.3	0.2
45°	Winter	*1.7*	*1.4*	*1.1*	0.8	0.6	0.5	0.3	0.2	0.2	0.1	0.1

Table 5. *The factor γ from equation (3.36), multiplied with 10^{10}. Radiation data according to Brewer & Wilson, and Johnson. D-limit at 3080 Å; at pressure levels to the left of the lines the time of restoration of ozone is less than 10 days*

Latitude	Season	Pressure in mb 5	6	7	8	9	10	12	14	16	18	20
0°		*1.9*	*1.4*	*1.1*	*0.9*	*0.8*	*0.6*	*0.5*	0.4	0.3	0.3	0.2
30°	Spring	*1.9*	*1.5*	*1.2*	*0.9*	*0.8*	*0.6*	0.5	0.4	0.3	0.2	0.2
30°	Summer	*2.3*	*1.7*	*1.3*	*1.0*	*0.9*	*0.8*	*0.6*	0.4	0.3	0.3	0.2
30°	Autumn	*1.8*	*1.4*	*1.1*	*0.9*	*0.7*	*0.6*	0.5	0.4	0.3	0.2	0.2
30°	Winter	*2.2*	*1.5*	*1.2*	*1.0*	*0.8*	0.6	0.4	0.3	0.2	0.2	0.1
45°	Spring	*1.8*	*1.3*	*1.0*	*0.8*	*0.6*	0.5	0.5	0.3	0.2	0.2	0.1
45°	Summer	*2.1*	*1.6*	*1.2*	*1.0*	*0.8*	*0.7*	*0.6*	0.4	0.4	0.3	0.2
45°	Autumn	*2.1*	*1.6*	*1.3*	*1.0*	*0.8*	*0.7*	0.5	0.3	0.3	0.2	0.2
45°	Winter	*1.6*	*1.2*	*0.9*	0.7	0.5	0.4	0.2	0.2	0.1	0.1	0.1

5.2.1. *The quantum efficiency data for reaction (2.2) given by De More and Raper (1962) are assumed to be correct. Reduction of ozone only by reactions (2.9) and (2.10)*

As can be seen from table 4 a satisfactory profile can only be obtained if the water vapour mixing ratio increases with a factor as large as 10 per scale height between 10 and 5 mb. Such a strong increase is very difficult to explain, requiring very short photochemical restoration times for the water vapour, and is also in contradiction to the observations by Houghton (1966) and Mastenbrook (1968), which indicate a constant mixing ratio $[H_2O]/[M] = 5 \times 10^{-6}$. There is therefore strong evidence to reject this alternative.

5.2.2. *De More and Raper's efficiency data. Constant water vapour mixing ratio in the stratosphere. Odd oxygen destruction also by reaction (2.13)*

Reactions (2.9) and (2.13) together cannot balance the production of odd oxygen at 30 km.

This would require that

$$\overline{k_{13}[O][O_2H]} = \bar{J}_2[O_2].$$

By use of expressions (3.8), (3.12), (3.15), (3.17), (3.24) and (5.2) it follows that this equality can be written as:

$$\frac{k_{13}\bar{J}_{3t}[O_3]}{k_6[O_2][M]} \sqrt{\frac{2}{\beta}\frac{k_8[H_2O]}{k_5[M]}\bar{J}_3^*[O_3]} = \bar{J}_2[O_2].$$

This equality is satisfied if for example

$$k_{13} = 5 \times 10^{-11},\ k_6 = 10^{-34},\ k_8 = 2 \times 10^{-10}.$$

It seems very improbable that such conditions are really fullfilled. It therefore seems necessary to require that reduction of odd oxygen at the 30 km level occurs via reactions (2.9) and (2.10).

The requirement of the strongly increasing water vapour mixing ratio with height from the previous alternative could now be removed if reaction (2.13) would be twice as effective as reaction (2.10) in reducing odd oxygen at 35 km. The desired conditions are approximately fulfilled if with Brewer-Wilson's data (1965) and $(H_2O]/[M] = 5 \times 10^{-6}$:

$$k_{10}\sqrt{k_8} = 2 \times 10^{-19}$$

$$\frac{k_{13}}{k_6 k_{10}} = 2 \times 10^{37}.$$

Because $k_8 < 2 \times 10^{-10}$ (collision frequency)

$$k_{10} > 10^{-14}$$

and because probably

$$k_{13} < 5 \times 10^{-11}$$

$$k_6 < 2 \times 10^{-34}.$$

A good profile can be obtained in this region when $k_{16} = 6 \times 10^{-34}$, $k_{10} = 5 \times 10^{-15}$, $k_{13} = 5 \times 10^{-11}$ and $[H_2O]/[M] = 2 \times 10^{-5}$. This choice of values gives however much too large destruction of odd oxygen at 50 km. The use of Detwiler *et al.* data (1961) does not make the situation better.

5.2.3. *Constant water vapor mixing ratio with altitude. De More and Raper's quantum efficiency data not adopted. Ozone reduction by reactions (2.9) and (2.10)*

A satisfying ozone profile can be obtained only if production of $O(^1D)$ by reaction (2.2) is negligible for wavelengths $\lambda \geq 2880$ Å (see table 1). However, in this case with the given water vapour particle mixing ratio 5×10^{-6} we have to require $k_{10} > 2 \times 10^{-13}$ which is an unrealistically large value. For this reason we have to disregard this alternative.

5.2.4. *OH- and O_2H-production by a different scheme*

Some attention should be given to the following possibility. For wavelengths shorter than 2240 Å ozone dissociation might give rise to excited molecular ozygen in the $^3\Sigma_u^+$ state. The following reactions replacing reactions (2.2), (2.5) and (2.8) in our photochemical scheme become of interest:

$$O_3 + h\nu \rightarrow O_2(^3\textstyle\sum_u^+) + O(^3P) \qquad (2.2\,a)$$

$$O_2(^3\textstyle\sum_u^+) + M \rightarrow O_2 + M \qquad (2.5\,a)$$

$$O_2(^3\textstyle\sum_u^+) + H_2O \rightarrow OH + O_2H. \qquad (2.8\,a)$$

All the deductions made before are with obvious modifications valid for this scheme. A scheme with ozone reduction by reactions (2.9), (2.10) and (2.13) (see 5.2.2) would fit the data quite well if

$$k_9^2 \frac{k_{8a}}{k_{5a}} = 10^{-25}$$

provided that reaction (2.2a) occurs with a

quantum efficiency = 1 Choosing $k_9 = 10^{-14}$ the last relation would give as requi rement

$$\frac{k_{8a}}{k_{5a}} = 10^3.$$

It is interesting to see that in this case the same wavelength range of radiation is responsible for the production and destruction of ozone.

5.3. Some concluding remarks

In terms of our knowledge of the parameters, it appears improbable that either the classical or the Hampson theory is in agreement with the ozone "Umkehr" observations in the altitude region 30–35 km. One can think of other alternatives than those treated here, as for example odd oxygen destruction by reactions (2.9), (2.10) and (2.13) and a D-limit of a shorter wavelength or a strong temperature dependence of the rate constants. However, also such alternatives yield conditions on the rate constants that are very improbable. Combination of the Hampson & Chapman theories could yield a satisfying profile, as can be seen from the study by Hesstvedt (1968), where reaction (2.7) is of greater importance at 35 km than at 30 km. The values of the rate constants k_6 and k_7 applied by Hesstvedt are, however, in disagreement with the latest laboratory values. An interesting point is also that ozone restoration times below 30 km in the Hampson theory may become much shorter than those in the classical theory for certain choices of the D-limit. Indeed, according to the original Hampson theory, the restoration time for the ozone, proportional to

$$\left(\frac{[H_2O]}{[M]}[O_3]J_3^*\right)^{-\frac{1}{2}},$$

would be a few days in the lower troposphere because of the large water vapour mixing ratios, if the D-limit is choosen to be 3100 Å. Such restoration times are much too short to be acceptable. To defend the theory, one therefore has to require in the troposphere processes much more efficient than reactions (2.15)–(2.17) for reduction of the concentrations of OH- and O_2H-molecules. One example of such processes could be the reaction

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

for which Schofield (1967) gives a rate coefficient $1.2 \times 10^{-10} \exp(-3000/T)$, while $[CH_4]/[M] = 1.5 \times 10^{-6}$.

6. Conclusions

In this investigation the photochemistry of the ozone in the stratosphere has been examined. Above 30 km in the summer and autumn seasons in low and middle latitudes the ozone concentrations are mainly functions of photochemical processes with no larger deviations from the photochemical equilibrium than 20 %. This was derived from the fact that meridional and vertical motions which are required to balance the influence of the photochemical processes on the ozone are larger than the motions which may be deduced from the observations. Therefore, as far down as the 30 km level, near balance must exist between production of odd oxygen by photodissociation of the molecular oxygen and destruction by other photochemical processes. Given the latest laboratory determinations of rate coefficients, reaction (2.7) cannot be the destruction reaction. Reduction by the chain of reactions (2.9)–(2.13) between 30 and 35 km is only possible if the rate coefficients k_6, k_8, k_{10} and k_{13} satisfy the numerical conditions given in section 5.2.2, which seems to be improbable. A complication may arise if our assumption with respect to the rate coefficients for reaction (2.18) is not valid.

With regard to the stratosphere as a whole it is obvious that in the search for an appropriate theory there is a strong need for laboratory determinations of the rate coefficients k_6, k_8, k_9, k_{10}, k_{13} and k_{18}. The electronic states of the products of the ozone dissociation in reactions (2.2) and (2.3) is also a matter of great interest. Other remaining questions are concerned with the solar flux data in the region from 2000–3000 Å, the absorption cross sections for molecular oxygen between 2000 and 2425 Å and the quantum efficiency data for reactions (2.1), (2.2) and (2.3). On the observational side there is a strong need for the development of new and improvement of existing techniques for directly and indirectly measuring concentrations of atmospheric constituents like $O(^3P)$, $O(^1D)$, O_3, OH, O_2H, H, H_2O, etc., in the stratosphere and mesosphere.

If the water vapour is of great importance for the ozone photochemistry a negative correlation should exist between water vapour and ozone concentrations. One could then possibly use the inexpensive ground based Umkehr data and rocket soundings on ozone concentrations as a tool for deducing some characteristics of at-

mospheric motions between 25 and 50 km in the atmosphere. The measured ozone concentrations may in this case be used to deduce variations in the water vapour mixing ratio, which between 25 and 50 km certainly is a more conservative property of the atmosphere than is the ozone and may be used as a tracer. The role of the water vapour in the energy budget of the stratosphere should be stressed. Larger water vapour concentrations cause smaller ozone concentrations and thus less absorption of solar ultraviolet radiation, together with a larger infrared cooling. The correlation between ozone concentrations and temperatures is thus expected to be positive.

In the classical photochemical theory for ozone, high temperatures (caused by dynamical processes) imply low ozone concentrations, because of the temperature dependence of k_6 and k_7. In those regions of the atmosphere where the time of restoration for ozone is short we might, according to the classical theory, expect a negative correlation between temperature and ozone concentrations. Combined measurements of temperature, ozone concentration and water vapour concentration at the same time would therefore be very useful.

In view of the results of this study it is conceivable that at least part of the solution of the problem of the ozone distribution might be given by the introduction of photochemical processes other than those treated here. The influence of nitrogen compounds on the photochemistry of the ozone layer should be investigated. In the first place observations on the concentrations of such gases in the stratosphere and needed. The role of aerosols in the photochemistry of the ozone is also an interesting matter.

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APPENDIX 1

Argument for the deletion of reaction (4)

According to Hampson's theory during photochemical equilibrium

$$\overline{[OH]} = \frac{\bar{J}_2[O_2]}{k_9[O_3]}. \qquad \text{(A1.1)}$$

In order to be allowed to neglect reactions (2.4) compared with reaction (2.18) we must satisfy the condition

$$k_{18}\overline{[OH]} \gg \bar{J}_4. \qquad \text{(A1.2)}$$

Equations (A1.1) and (A1.2) then yield

$$\frac{k_{18}\bar{J}_2[O_2]}{k_9[O_3]} \gg \bar{J}_4. \qquad \text{(A1.3)}$$

Inserting known values of $\bar{J}_2$ and $\bar{J}_4$ (Hesstvedt, 1968) and the assumed values of k_9 and k_{18} (see (2.24) and (2.26)) we see that (A1.3) is satisfied.

APPENDIX 2

Ozone and temperature data

Direct measurements of ozone concentrations above 30 km are still very scarce. Only a small part of the direct balloon-borne chemical measurements (Hering, 1964), (Hering-Borden, 1964, 1965, 1967), (Komhyr-Sticksel, 1967) reach this region. Thus still the only statistics of ozone data appropriate for this study are the Umkehr data. The ozone concentrations used in this work are according to Dütsch & Mateer (1964). The following stations have been assumed to be representative of their respective latitude circles:

Table 6. *Partial pressure of ozone (in μmb) used in this work*

Pressure in mb	Season Latitude 0°	30° Spring	30° Summer	30° Autumn	30° Winter	45° Spring	45° Summer	45° Autumn	45° Winter
1	3	3	3	3	3	3	3	3	3
2	9	10	12	13	11	10	9	10	10
3	19	19	19	22	19	20	20	20	20
4	29	30	28	32	25	30	30	27	27
5	40	40	36	40	33	38	38	34	33
6	49	47	46	49	42	46	47	41	38
7	58	57	56	58	48	55	56	48	44
8	66	65	64	67	55	63	63	56	51
9	75	73	71	74	63	70	70	63	58
10	85	80	78	82	72	76	77	69	64
12	102	92	94	94	87	87	87	80	78
14	115	103	105	103	97	96	96	90	88
16	123	110	113	110	106	103	103	100	94
18	129	116	120	117	113	110	106	105	102
20	133	121	123	122	117	116	111	110	108

for 0°: Leopoldville
for 30°: Kagoshima
for 45°: Arosa.

The above mean values for the atmospheric layers used in their Umkehr evaluations were plotted on ozonograms so that ozone concentrations for the pressure levels used in this investigation could be determined by interpolation or extrapolation (see Table 6).

Of course, the question remains of how well these mean ozone Umkehr observations represent the real mean ozone concentrations. Comparisons between concentrations obtained with the indirect Umkehr method and the direct balloon-borne chemical methods have been made by Mateer & Dütsch (1964). Results for the altitude region 25–35 km show deviations which are only on the order of 10%. Even if we assumed the applied "Umkehr" data as being in error by 20% the conclusions drawn in this paper would not be essentially altered. Only the numerical values obtained would be somewhat changed. Above 35 km comparisons can be made between the Umkehr data and the data obtained from rocket ascents. This is, however, very difficult, because of the uncertainties inherent in the rocket measurements as evidenced by the large deviations between the observations.

The temperatures that were used have been taken from Handbook of Geophysics and Space Environments (1965).

APPENDIX 3

The numerical approximation

The computations were accomplished by the CDC 3600 computer. The wavelength steps $d\lambda$ used in the wavelength-integrations were as follows:

from 1800–2425 Å: $d\lambda = 25$ Å
from 2425–3500 Å: $d\lambda = 10$ Å
from 4000–11 800 Å: $d\lambda = 100$ Å

For wavelengths less than 2425 Å, the solar fluxes and absorption coefficients recommended by Brewer & Wilson (1965) were used and were assumed to be constant in the 25 Å intervals. For wavelengths greater than 2425 Å, the values of solar fluxes and absorption coefficients applicable for the middle of the intervals considered

were applied. It was, therefore, sometimes necessary to interpolate between values given in the literature. In view of the short wavelength steps used in evaluating the integrals, it is felt that differences between the calculated values of dissociation rates in this research and the actual values occurring in nature are small, provided experimental data accurately reflect natural processes. Time integrations of J_2, J_3, $\sqrt{J_3^*}$ to obtain $\bar{J}_2, \bar{J}_3$ and $\sqrt{\bar{J}_3^*}$ were accomplished with a time step of 10 minutes. The times of sunrise and sunset used in this paper are the times applicable at the earth's surface. With regard to $\bar{J}_3$, this means that the calculated value is somewhat smaller than the actual value. Because of the small depletion of the solar radiation in the visible, a contribution to $\bar{J}_3$ in the Chappuis band of ozone will also occur before sunrise and after sunset, since the upper atmosphere is still illuminated by solar radiation. Also, a contribution to the value of $\bar{J}_3$ will normally be made by scattering from below, that is, by clouds in the troposphere and by Rayleigh scattering. The time step used is certainly short enough to obtain good accuracy. When calculations were accomplished to determine the effect of scattered radiation, a time step of 60 minutes had to be used because of the large computation time required. The direct radiation terms above 40 km when calculated with this latter time step never deviated more than 20% from the calculated values using a 10 minute time step, and below 40 km the deviation was even smaller.

To do the height integrations the atmosphere was divided into pressure layers with the following pressure steps dp:

1–10 mb: $dp = 1$ mb
10–20 mb: $dp = 2$ mb
20–35 mb: $dp = 3$ mb
35–60 mb: $dp = 5$ mb
60–100 mb: $dp = 10$ mb.

The above division means that except for the upper part between 1 mb and 5 mb, the atmosphere has been divided into layers of about 1 km in thickness. Inside the layers the ozone mixing ratio has been assumed to be constant and given by an appropriate mean value.

Optical thicknesses above the 1 mb level are calculated with the assumption that $[O_3]\,(p) = [O_3]\,(1)\,p^{\frac{3}{2}}$, where p is the pressure in mb.

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ОПРЕДЕЛЕНИЕ ПАРАМЕТРОВ, ПОЯВЛЯЮЩИХСЯ В »СУХОЙ» И »ВЛАЖНОЙ» ФОТОХИМИЧЕСКИХ ТЕОРИЯХ СТРАТОСФЕРНОГО ОЗОНА

Анализируются существующие фотохимические теории стратосферного озона. Показано, что концентрация озона выше 30 *км* между 0 и 45° широты летом определяется в основном фотохимическими процессами.

Параметры, появляющиеся в теории озона Чэпмана и Хэмпсона определяются подгонкой их к средним концентрациям озона, полученным путем метода обращения. Полученные результаты показывают, что маловероятно, чтобы какая-нибудь одна из вышеупомянутых теорий могла бы объяснить наблюдаемые распределения озона. Даны количественные условия на критические параметры. Обсуждается также некоторая альтернативная теория, где рассматривается диссоциация водяного пара возбужденным молекулярным кислородом.