On the determination of characteristic times in a pure oxygen atmosphere

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ABSTRACT

In a pure oxygen atmosphere, daytime equilibrium concentrations of O, O_2 and O_3 were calculated for heights from 30 to 140 km and for three temperature profiles: low latitude, high latitude summer, and high latitude winter. The results agree with ozone measurements up to 70 km. Expressions for restoration of photochemical equilibrium were developed. These consist of two exponential terms with widely different characteristic times. The relative importance of these terms depends upon the character of the initial perturbation.

1. Introduction

Since CHAPMAN (1930) discovered the nearly complete dissociation of O_2 above 100 km, various model atmospheres have been developed to show the height distribution of the concentrations of the three allotropes of oxygen: O, O_2 and O_3. The simplest model is a pure oxygen atmosphere in photochemical equilibrium, where only O, O_2 and O_3 are allowed to react chemically, where no diffusion takes place, and where the solar radiation does not vary with time. Such model atmospheres, which have been computed by PENNDORF (1949), BATES and NICOLET (1950) and others, are believed to give a fairly representative picture of the height distribution in a sunlit atmosphere of the three oxygen allotropes.

Only one series of direct measurements has been made to verify the theoretical results. JOHNSON *et al.* (1952) measured the concentration of ozone up to 70 km. Their results agree very well with the theoretically computed values. Therefore, the assumption of photochemical equilibrium is believed to give an accuracy in the determination of the concentrations which is sufficient for many problems.

However, departures from daytime photochemical equilibrium occur, partly as a result of the motion of the air, partly as a result of diurnal and seasonal variations in the solar radiation. Expressions for the night-time variation of the concentrations of O and O_3 were developed by PENNDORF (1949) and by BATES and NICOLET (1950). Departures from, and characteristic times for restoration of photochemical equilibrium for ozone were first studied by WULF and DEMING (1937). Later, time variations in an O–O_2 atmosphere were investigated by PENNDORF (1949). The more complete O–O_2–O_3 atmosphere was first treated by BATES and NICOLET (1950). The results have been worked out in more detail, but along the same lines as in earlier works, by NICOLET (1958).

The characteristic times for restoration of photochemical equilibrium are obtained from the integrated form of the differential equations (3.1–3.3). In earlier works these equations have been simplified, partly by omitting terms which were believed to be of minor importance, partly by regarding some of the variables as constants. With such simplifications the solutions can only be regarded as approximations, in most cases very useful ones. But in many cases this procedure leads to wrong results, especially for the levels around 60 km.

It is the aim of this paper to show how the general case may be treated by linearizing the equations. Consequently, the results obtained below are valid only for small departures from the equilibrium concentrations. The difference between the results obtained below and the

[1] Most of the work reported in this study was done during a stay at the International Meteorological Institute, Stockholm.

earlier ones is not such that our general picture of the time variations in an oxygen atmosphere is altered. However, it is shown that the characteristic times should be given as a sum of two exponential terms, the relative importance of which depends upon the magnitude of the initial departures from equilibrium concentrations.

2. The model atmospheres

A pure oxygen model atmosphere is defined by the selection of photochemical reactions which are allowed to take place, by the choice of temperature profile and by the intensity of the dissociating solar radiation, i.e. by the elevation of the sun. In this paper we shall follow earlier writers and assume that the distribution of oxygen upon O, O_2 and O_3 is determined by the reactions

$$O_2 + h\nu \rightarrow O + O \quad (J_2) \tag{2.1}$$

$$O_3 + h\nu \rightarrow O + O_2 \quad (J_3) \tag{2.2}$$

$$O + O + M \rightarrow O_2 + M \quad (k_1 = 5 \times 10^{-34} T^{-\frac{1}{2}} \text{cm}^6/\text{sec}) \tag{2.3}$$

$$O + O_2 + M \rightarrow O_3 + M \quad (k_2 = 5 \times 10^{-36} T^{-\frac{1}{2}} \text{cm}^6/\text{sec}) \tag{2.4}$$

$$O + O_3 \rightarrow 2O_2 \quad (k_3 = 1.5 \times 10^{-11} T^{\frac{1}{2}} e^{-6/RT} \text{cm}^3/\text{sec}) \tag{2.5}$$

The concentrations of the non-reacting third-bodies (M) as well as the values of the rate coefficients k_1, k_2 and k_3 depend upon the selection of temperature profile. In this paper three different profiles will be considered, representing conditions in low latitudes and in high latitudes for summer and for winter. Up to 90 km the temperatures and pressures given by NORBERG and STROUD (1961) have been used (with a revision for high latitude winter, above 70 km). Above 100 km the data were taken from the U.S. Standard Atmosphere (SISSENWINE, DUBIN and WEXLER, 1962). The temperatures used are given in Table 1.

The dissociation rate coefficients, J_2 for molecular oxygen and J_3 for ozone, depend upon the absorption of solar radiation in the overlying part of the atmosphere, i.e. upon the temperature profile and upon the sun's elevation. In our three model atmospheres we have assumed the sun to be in zenith in low latitudes and at an elevation of 53½° (summer) and 6½° (winter) in high latitudes. Seasonal changes in the photochemical equilibrium concentrations are likely to be very small in low latitudes, while in higher latitudes a seasonal variation will occur, partly due to the marked temperature changes, partly due to the change in optical thickness passed by the sun's rays to reach a given level. In the computations, J_2 and J_3 will be regarded as constants, independent of perturbations in the overlying part of the atmosphere.

TABLE 1. *Adopted temperature profiles.*

Height, km	Low latitude, summer and winter	High latitude, summer	High latitude, winter
140	712°K	712°K	712°K
130	531	531	531
120	349	349	349
110	257	257	257
100	218	212	246
90	190	180	235
80	190	170	215
70	219	212	225
60	247	254	252
50	270	275	259
40	254	254	230
30	233	234	200

3. Equilibrium concentrations

On the basis of the reactions (2.1) to (2.5) it is now possible to develop expressions for the rate of change of the concentrations of the oxygen allotropes. Let the concentrations of O, O_2 and O_3 be denoted by x, y and z and the total particle concentration by m. The rates of change are then given by

$$\frac{dx}{dt} = 2J_2 y + J_3 z - 2k_1 m x^2 - k_2 m x y - k_3 x z, \tag{3.1}$$

$$\frac{dy}{dt} = k_1 m x^2 + 2k_3 x z + J_3 z - J_2 y - k_2 m x y, \tag{3.2}$$

$$\frac{dz}{dt} = k_2 m x y - J_3 z - k_3 x z. \tag{3.3}$$

Assuming the total amount of oxygen to be a

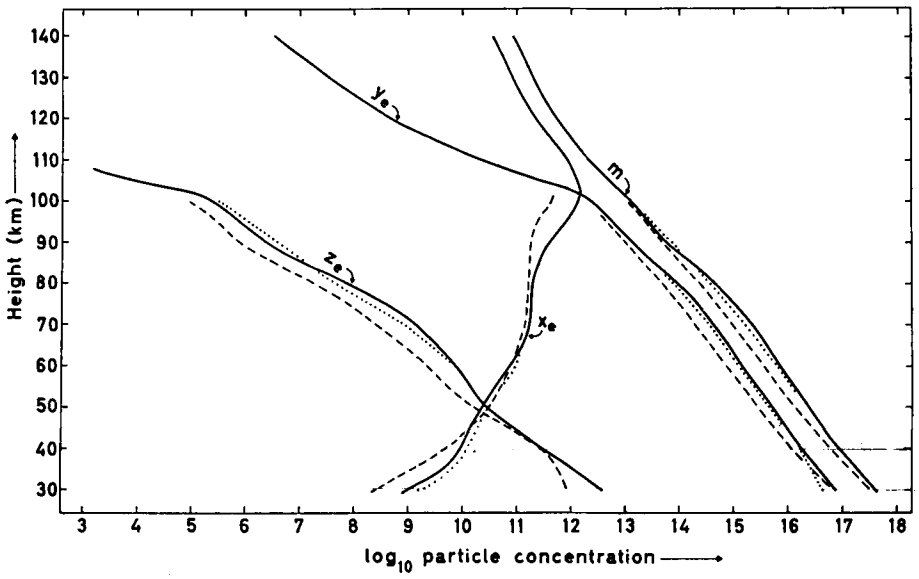

FIG. 1. Concentrations of atomic oxygen (x_e), molecular oxygen (y_e) and ozone (z_e) in photochemical equilibrium in a sunlit atmosphere. Air particle concentrations are shown by the curves m. (——= high latitude summer; – – – = high latitude winter; · · · · = low latitude).

constant, one of the equations (3.1) to (3.3) may be replaced by

$$\frac{x}{2} + y + \frac{3z}{2} = 0.2095\ m. \qquad (3.4)$$

A determination of the characteristic times in the oxygen model atmosphere depends upon the knowledge of the equilibrium concentrations x_e, y_e and z_e. These are obtained by putting $dx/dt = dy/dt = dz/dt = 0$ in (3.1) to (3.3). From (3.3) we then get

$$z_e = \frac{k_2 m x_e y_e}{J_3 + k_3 x_e}. \qquad (3.5)$$

Substitution of (3.5) in (3.1) gives an equation of the third degree. For all practical purposes the positive root of this equation in x_e may be expressed as

$$x_e^2 = \frac{J_2 y_e}{k_1 m} \cdot \left(1 + \frac{k_2 k_3 y_e}{k_1 J_3}\right)^{-1}. \qquad (3.6\,a)$$

At 70 km and above the ratio $k_2 k_3 y_e / k_1 J_3$ is much smaller than unity. (3.6a) then reduces to

$$x_e^2 = \frac{J_2 y_e}{k_1 m} \quad \text{(above 70 km)}. \qquad (3.6\,b)$$

Below 55 km the ratio $k_2 k_3 y_e / k_1 J_3$ is much larger than unity, and (3.6a) takes the form

$$x_e^2 = \frac{J_2 J_3}{k_2 k_3 m} \quad \text{(below 55 km)}. \qquad (3.6\,c)$$

The values x_e, y_e and z_e may now be computed for different levels and for the three model atmospheres described in section 2. The results are illustrated in Fig. 1. It turns out that the magnitude of the seasonal and latitudinal variations is never such that the determination of the characteristic times will be seriously complicated by using different temperature profiles.

4. Characteristic times in a sunlit atmosphere

We shall consider a departure from day-time equilibrium. Substitution of

$$\left.\begin{aligned} x &= x_e + x' \\ y &= y_e + y' \\ z &= z_e + z' \end{aligned}\right\} \qquad (4.1)$$

into equation (3.1) to (3.3) gives

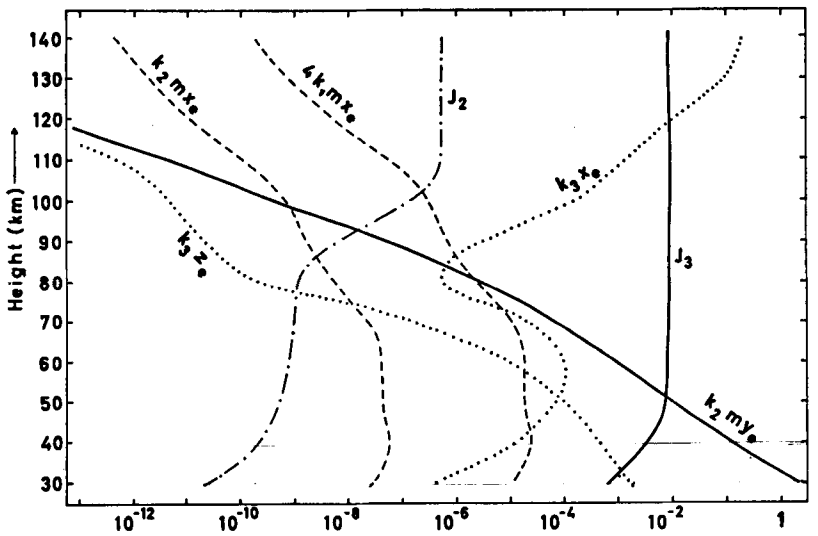

FIG. 2. Variation with height of the different quantities occurring in the expressions (4.6) and (4.7) for a and b.

$$\left.\begin{aligned}
&\left(4k_1 mx_e + k_2 my_e + k_3 z_e + \frac{d}{dt}\right) x' \\
&\qquad + (k_2 mx_e - 2J_2) y' + (k_3 x_e - J_3) z' = 0 \\
&(k_2 my_e - 2k_1 mx_e - 2k_3 z_e) x' \\
&+ \left(k_2 mx_e + J_2 + \frac{d}{dt}\right) y' - (J_3 + 2k_3 x_e) z' = 0 \\
&(k_3 z_e - k_2 my_e) x' - k_2 mx_e \cdot y' \\
&\qquad + \left(J_3 + k_3 x_e + \frac{d}{dt}\right) z' = 0,
\end{aligned}\right\} \quad (4.2)$$

where the second order terms in the perturbations x', y' and z' have been neglected. This means that we shall restrict ourselves to the consideration of perturbations which are small in comparison to the equilibrium values. If we write

$$\left.\begin{aligned}
x' &= A_1 e^{-\lambda_1 t} + B_1 e^{-\lambda_2 t} \\
y' &= A_2 e^{-\lambda_1 t} + B_2 e^{-\lambda_2 t} \\
z' &= A_3 e^{-\lambda_1 t} + B_3 e^{-\lambda_2 t},
\end{aligned}\right\} \quad (4.3)$$

λ_1 and λ_2 may be determined as the two roots (different from zero) of the equation

$$\begin{vmatrix}
(-\lambda + 4k_1 mx_e + k_2 my_e + k_3 z_e) & (k_2 mx_e - 2J_2) & (k_3 x_e - J_3) \\
(k_2 my_e - 2k_1 mx_e - 2k_3 z_e) & (-\lambda + k_2 mx_e + J_2) & (-J_3 - 2k_3 x_e) \\
(k_3 z_e - k_2 my_e) & -k_2 mx_e & (-\lambda + J_3 + k_3 x_e)
\end{vmatrix} = 0 \quad (4.4)$$

Equation (4.4) may be written

$$\lambda^2 - a\lambda + b = 0, \quad (4.5)$$

where

$$a = J_2 + J_3 + k_3 x_e + k_2 mx_e + 4k_1 mx_e + k_2 my_e + k_3 z_e \quad (4.6)$$

and

$$\begin{aligned}
b = {} & J_3(J_2 + 4k_1 mx_e + 2k_3 z_e) \\
& + k_3 x_e(J_2 + 4k_1 mx_e - k_2 mx_e + 2k_2 my_e) \\
& + 3J_2(k_2 my_e - k_3 z_e) \\
& + 3k_2 mx_e(2k_1 mx_e + k_3 z_e).
\end{aligned} \quad (4.7)$$

In order to solve (4.5) we must compute all the terms occurring in (4.6) and (4.7). The relative importance of these terms is shown in Fig. 2. It follows that the constants a and b may be expressed as

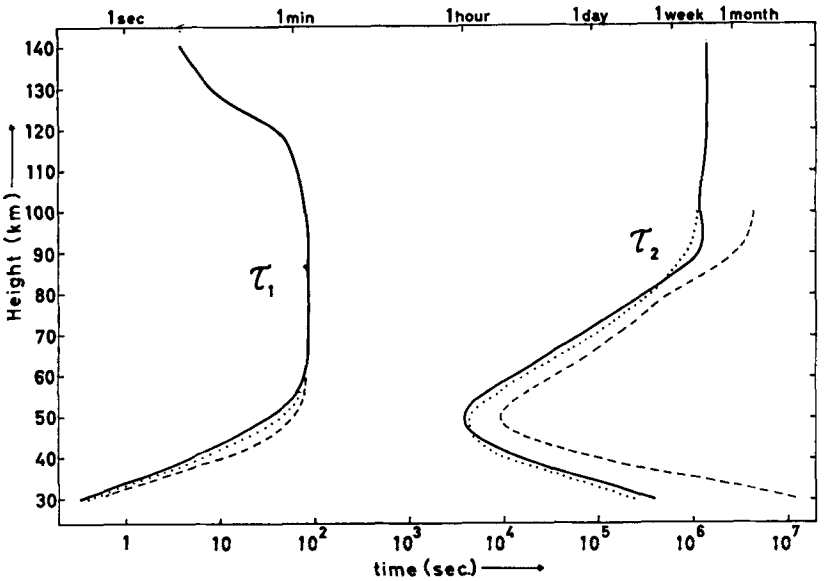

FIG. 3. Characteristic times τ_1 and τ_2 for the two exponential terms in the expressions (4.19a–c) for the perturbations x', y' and z'.

$$a = J_3 + k_3 x_e + k_2 m y_e \tag{4.8}$$

and

$$B = J_3(J_2 + 4k_1 m x_e + 2k_3 z_e) + k_3 x_e(J_2 + 4k_1 m x_e + 2k_2 m y_e) \tag{4.9}$$

without serious approximation.

Since the ratio $4b/a^2$ is much smaller than unity (in fact its maximum value is about $4 \cdot 10^{-2}$), the solutions of (4.5) are, with a very high degree of accuracy

$$\lambda_1 = a = J_3 + k_2 m y_e + k_3 x_e$$

$$\lambda_2 = \frac{b}{a} = \frac{J_3(J_2 + 4k_1 m x_e + 2k_3 z_e) + k_3 x_e(J_2 + 4k_1 m x_e + 2k_2 m y_e)}{J_3 + k_2 m y_e + k_3 x_e}. \tag{4.10}$$

This means that equation (4.4) has two real, positive roots, which again means that the perturbations converge to zero without oscillations. For the A-terms and the B-terms in (4.3) we may define characteristic times, $\tau_1 = ln\ 2/\lambda_1$ and $\tau_2 = ln\ 2/\lambda_2$, indicating the time it takes for that term to be reduced to 50% of its initial value. The variations of these two functions with height are shown in Fig. 3. It is important to notice that τ_1 and τ_2 for all levels differ by orders of magnitude.

If we want to study the conditions at a specified level, the general expressions (4.10) for λ_1 and λ_2 may be simplified considerably:

110–140 km: $\lambda_1 = J_3 + k_3 x_e$,

$\lambda_2 = J_2$;

100 km: $\lambda_1 = J_3 + k_3 x_e$,

$\lambda_2 = J_2 + 4k_1 m x_e$;

70–90 km: $\lambda_1 = J_3$,

$\lambda_2 = 4k_1 m x_e = 4\sqrt{J_2 k_1 m y_e}$;

50–60 km: $\lambda_1 = J_3 + k_2 m y_e$,

$\lambda_2 = 4\dfrac{J_3 k_1 m x_e + k_2 m y_e k_3 x_e}{J_3 + k_2 m y_e}$;

40 km: $\lambda_1 = J_3 + k_2 m y_e \approx k_2 m y_e$,

$\lambda_2 = 4k_3 x_e \cdot \dfrac{k_2 m y_e}{J_3 + k_2 m y_e} \approx 4k_3 x_e$;

below 35 km: $\lambda_1 = k_2 m y_e$,

$\lambda_2 = 4k_3 x_e = 4\sqrt{k_3 J_2 J_3 / k_2 m}$.

We shall next determine the coefficients A_1, A_2, A_3 and B_1, B_2, B_3 in (4.3). Substitution of (4.3) in (4.2) gives three equations of the form

$$C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} = 0. \qquad (4.12)$$

Since these equations are valid for all values of t, we must have $C_1 = C_2 = 0$. This gives two sets of equations, one relating A_1, A_2 and A_3:

$$(4k_1 m x_e + k_2 m y_e + k_3 z_e - \lambda_1) A_1 + (k_2 m x_e - 2J_2) A_2 + (k_3 x_e - J_3) A_3 = 0, \qquad (4.13a)$$

$$(k_2 m y_e - 2k_1 m x_e - 2k_3 z_e) A_1 + (k_2 m x_e + J_2 - \lambda_1) A_2 - (J_3 + 2k_3 x_e) A_3 = 0, \qquad (4.13b)$$

$$(k_3 z_e - k_2 m y_e) A_1 - k_2 m x_e \cdot A_2 + (J_3 k_3 x_e - \lambda_1) A_3 = 0, \qquad (4.13c)$$

and a similar one relating B_1, B_2 and B_3. (We only have to replace λ_1, A_1, A_2 and A_3 by λ_2, B_1, B_2 and B_3.) If we assume the total amount of oxygen at a level to be constant, we have

$$x' + 2y' + 3z' = 0 \qquad (4.14)$$

for all values of t. Consequently

$$A_1 + 2A_2 + 3A_3 = B_1 + 2B_2 + 3B_3 = 0 \qquad (4.15)$$

Substitution of A_1 in equation (4.13a) gives

$$\frac{A_2}{A_3} = -\left(1 + \frac{k_3 x_e}{J_3 + k_3 x_e + 3k_2 m y_e}\right). \qquad (4.16)$$

Hence, we may write with sufficient accuracy

$$A_1 = -\tfrac{1}{2} A_2 = A_3 \quad \text{above 130 km,} \qquad (4.17a)$$

$$A_2 = -\frac{J_2}{J_3} A_1 = -\frac{3}{2} A_3 \quad \sim 120 \text{ km,} \qquad (4.17b)$$

$$A_1 = A_2 = -A_3 \quad \text{below 110 km.} \qquad (4.17c)$$

The ratio A_2/A_3 undergoes a rapid change with height (from -1 at 110 km to -2 at 130 km) where the expression $J_3 - k_3 x$ changes sign, passing through the value zero at about 120 km. From (4.15) and the equation analogous to (4.13c) we obtain upon substitution of (3.5)

$$\frac{B_2}{B_3} = -\frac{J_3 + k_3 x_e + 3k_2 m y_e}{2k_2 m y_e - k_2 m x_e} = -\frac{3 + (x_e/z_e)}{2(1 - [x_e/2y_e])} \qquad (4.18a)$$

and

$$\frac{B_1}{B_2} = \frac{2(J_3 + k_3 x_e)}{2k_2 m y_e - k_2 m x_e} = \frac{x_e/z_e}{1 - (x_e/2y_e)}. \qquad (4.18b)$$

A_1, A_2, A_3, B_1, B_2 and B_3 can now finally be expressed in terms of the initial values of the perturbations, x_0', y_0' and z_0', which are obtained by putting $t = 0$ in (4.3). Since the relationships between the coefficients B_1, B_2 and B_3 are relatively complicated, we shall, for the sake of simplicity, in the following restrict ourselves to the consideration of levels up to 100 km. Since $x_e < 2y_e$, the expressions (4.18a–b) may be simplified. The following formulae are obtained

$$x' = \frac{z_e x_0' - x_e z_0'}{x_e + z_e} e^{-\lambda_1 t} + \frac{x_e (x_0' + z_0')}{x_e + z_e} e^{-\lambda_2 t}, \qquad (4.19a)$$

$$y' = \frac{z_e x_0' - x_e z_0'}{x_e + z_e} e^{-\lambda_1 t} - \frac{(x_e + 3z_e)(x_0' + z_0')}{2(x_e + z_e)} e^{-\lambda_2 t}, \qquad (4.19b)$$

$$z' = \frac{x_e z_0' - z_e x_0'}{x_e + z_e} e^{-\lambda_1 t} + \frac{z_e (x_0' + z_0')}{x_e + z_e} e^{-\lambda_2 t}. \qquad (4.19c)$$

Since $x_0' + 2y_0' + 3z_0' = 0$ we may easily express the coefficients in (4.19a–c) in terms of (x_0', y_0') or (y_0', z_0') instead of (x_0', z_0').

If we want to study the conditions at a specified level, the expressions (4.19a–c) may be simplified considerably. In the ozonosphere, for instance, $z_e > x_e$, and

$$z' = \left(\frac{x_e}{z_e} z_0' - x_0'\right) e^{-k_2 m y_e t} + (x_0' + z_0') e^{-4k_3 x_e t}. \qquad (4.20)$$

The values of z' for $t = \tau_1$ and $t = \tau_2$ are

$$z'_{\tau_1} \approx z_0' + \tfrac{1}{2} x_0' \qquad (4.21a)$$

and

$$z'_{\tau_2} \approx \tfrac{1}{2}(z_0' + x_0') \qquad (4.21b)$$

Strictly, our mathematical procedure is only valid for small departures from equilibrium. But even if we take the liberty to use (4.20) for larger values of x_0', the perturbations in atomic oxygen concentration are unlikely to be

so high that it will be comparable to the perturbations in ozone concentration, unless these, relative to the ozone equilibrium concentration, are so small that the problem is of academic interest only. Consequently, in most cases τ_2 may be regarded as the characteristic time for restoration of photochemical equilibrium in the ozonosphere, in agreement with the results obtained in earlier works. (If the initial perturbation of ozone is much smaller than that of atomic oxygen, we have

$$z_0' = x_0'(e^{-4k_2x_e t} - e^{-k_3 m y_e t}). \qquad (4.22)$$

After less than one minute the second term in the parenthesis has become negligibly small. Atomic and molecular oxygen recombine to form ozone, thus causing an increase in the departure from photochemical equilibrium. The restoration of equilibrium is then determined by the first term in the parenthesis in (4.22). Accordingly, even in this case, τ_2 indicates the characteristic time for ozone in the ozonosphere.)

A simplified discussion of a similar kind may be carried through for atomic (and molecular) oxygen for the levels above 60 km. In agreement with the results obtained in earlier works, τ_2 may, in the cases of greatest interest to us, be regarded as the characteristic time for restoration of photochemical equilibrium for atomic and molecular oxygen.

Concluding remarks

From what was found above, the characteristic times for O, O_2 and O_3 at a given level cannot be given by one fixed time. Since the restoration of photochemical equilibrium in a sunlit atmosphere is governed by two exponential terms, the characteristic times will depend upon the relative magnitudes of the initial disturbances. In the lowest and highest part of the interval studied (30–140 km), the results obtained in earlier works hold for the two allotropes having the largest concentrations. But for the third component, and throughout for levels around 50 km, more complicated expressions must be used to characterize the restoration of photochemical equilibrium.

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