

## A THEORETICAL TWO-DIMENSIONAL MODEL FOR MINOR CONSTITUENTS BELOW 50 KM

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## 1. INTRODUCTION

The ozone distribution in the atmosphere has been investigated for many years as well by experimental as by theoretical means. The basic facts about the latitudinal distribution of the ozone content became known by the work of Dobson et al (1920) and the first theory on the photo-chemistry of  $O_3$  in the atmosphere has been published by Chapman (1930) who considered the production and destruction mechanisms only in a pure oxygen atmosphere. If during two decades this theory seemed quite adequate to explain the observed vertical distribution of ozone and especially the maximum of its concentration in the middle of the stratosphere, it was later understood (see e.g. Bates and Nicolet, 1950) that atmospheric hydrogen compounds could not be omitted in the analysis of the problem since hydroxyl and hydroperoxyl radicals could remove odd oxygen particles.

The first theory of nitrogen oxides in the atmosphere has been established about 20 years before the first observational evidence of its presence in the stratosphere was suggested (see e.g. Nicolet, 1945 ; Bates 1952 ; Nicolet, 1955). But because of the lack of data concerning especially various rate constants, it was pointed out only in the beginning of the 70's (Crutzen, 1970 ; Johnson, 1971) that also nitrogen oxides could control the ozone distribution. In the recent years, theoretical models have been established in order to determine the vertical distribution of  $\text{NO}_x$  in the stratosphere (see e.g. Brasseur and Nicolet, 1973, Crutzen, 1973 ; McConnell and Mc Elroy, 1974) and to estimate its influence on the ozone profile (see e.g. Crutzen, 1970 ; Shimazaki and Ogawa, 1974 ; Mc Elroy et al. 1974).

The purpose of this paper is to present preliminary results of a steady state two-dimensional model for minor constituents. The effect of the dynamics will be simulated by three components of the eddy diffusion tensor and the distribution of nitrogen oxides will be parameterized according to its observation. The hydrogen compounds distribution will be calculated.

## 2. PHOTOCHEMISTRY

The aeronomical conditions of ozone are very different at the various stratospheric altitudes. If photochemical equilibrium conditions can be accepted at the stratopause level, they must be rejected in the lower stratosphere where the time to reach equilibrium conditions becomes large compared with the residence time of stratospheric particles. Therefore, the transport processes play the dominant role and, in the lower stratosphere and troposphere, the distribution of ozone mainly depends on the dynamical conditions of the atmosphere.

Systematical observations by a station network in the world or by Nimbus satellites (Prabhakara et al., 1971) have clearly established the existence of a latitudinal and seasonal variation of total ozone. The ozone column is of the order of 0.25 cm STP in the equatorial regions, twice as much in the winter high latitude regions and about 0.40 cm STP in the summer polar regions.

The photochemistry of ozone in the stratosphere has already been discussed in the overview papers on this question by Nicolet. (1970 and 1974). For that reason, only the most important reactions will be reminded here (fig. 1) and their adopted rate constants are given in table 1.

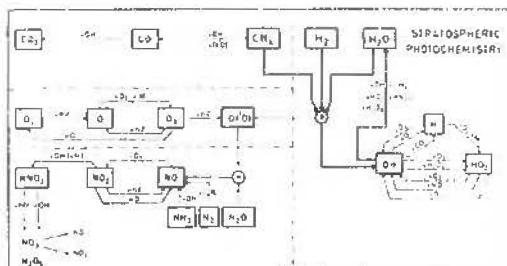
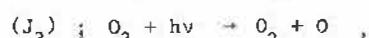
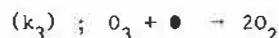
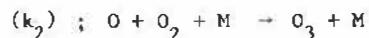
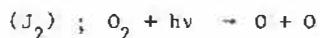


Fig. 1. Diagram of the most important reactions in the stratosphere

Considering the Chapman reaction scheme which considers a pure oxygen atmosphere,



the kinetic equations for ozone and atomic oxygen are

$$\frac{dn(O_3)}{dt} + k_3 n(O) n(O_3) + J_3 n(O_3) = k_2 n(M) n(O) \quad (1)$$

$n(O_2)$

and

$$\frac{dn(O)}{dt} + k_2 n(M) n(O) n(O_2) + k_3 n(O) n(O_3) = 2 J_2 n(O_2) + J_3 n(O_3) \quad (2)$$

Since atomic oxygen is almost immediately in photochemical equilibrium with ozone in the whole stratosphere, one can write with a fairly good approximation for  $O^3P$

$$n(O) = \frac{J_3 n(O_3)}{k_2 n(M) n(O_2)} \quad (3)$$

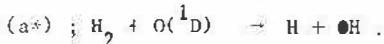
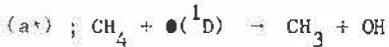
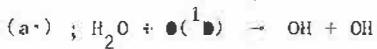
The behavior of ozone is entirely different since, below 25-30 km, it becomes more and more sensitive to the transport processes and therefore one must write the complete continuity equation

$$\frac{\partial n(O_3)}{\partial t} + \vec{V} \cdot \vec{\nabla} n(O_3) = 2 J_2 n(O_2) - \frac{k_3 J_3 n^2(O_3)}{k_2 n(M) n(O_2)}, \quad (4)$$

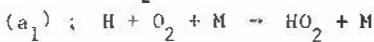
where  $\vec{\nabla}(O_3)$  is the particle flux of ozone which has to be determined from a transport equation.

The introduction of hydrogen compounds by Bates and Nicolet (1950) has shown a possible action of the hydroxyl and hydroperoxyl radicals on odd oxygen particles. Different authors (see e.g. Nicolet, 1970; Hesstvedt, 1968; Crutzen, 1971) have investigated the "wet" atmosphere at mesospheric altitudes. Also in the stratosphere, the effect of  $HO_x$  has to be considered.

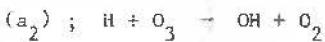
The production of hydroxyl radicals is due in the mesosphere to the photodissociation of water vapor but, in the stratosphere, it is caused by the oxidation process of water vapor, methane and molecular hydrogen by atomic oxygen in its electronically excited  ${}^1D$  state :



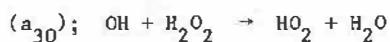
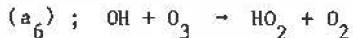
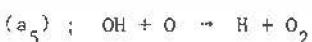
The lifetime of hydrogen atoms below 80 km is short since H immediately reacts with molecular oxygen  $O_2$  and a third body M to form hydroperoxyl radicals  $HO_2$



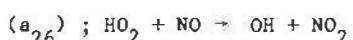
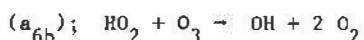
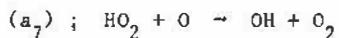
and with ozone to produce OH



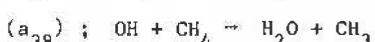
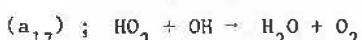
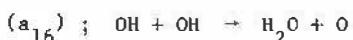
Hydroxyl radicals are destroyed by atomic oxygen in the upper stratosphere, by ozone in the middle and lower stratosphere and by carbon monoxide near and below the tropopause level; hydrogen peroxide could also play a role :



Hydroperoxyl radicals which are produced mainly by reactions (a<sub>1</sub>) and (a<sub>2</sub>) are destroyed by atomic oxygen above 35 km, by ozone in the middle and lower stratosphere and by nitric oxide below 20 km if its concentration is sufficiently high,



Finally, net loss processes for  $HO_x$  radicals have to be introduced in order to determine the effective balance of hydrogen compounds. The following reactions lead to the reformation of water vapor :



An analysis of the relative rates of these three reactions indicates that reaction (a<sub>17</sub>) has to be dominant if the value of rate constant  $a_{17} = 2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  is correct or only slightly overestimated. In this presentation, the effect of  $HNO_3$  is not introduced but it should be kept in mind that nitric acid could remove or produce OH (see reactions b<sub>22</sub>, b<sub>27</sub> and J<sub>HNO<sub>3</sub></sub> below). Considering these most important processes, the ratio between the  $HO_2$  and OH concentration is given by

$$\frac{n(HO_2)}{n(OH)} = \frac{a_5 n(O) + a_{36} n(CO)}{a_7 n(O) + a_{6b} n(O_3) + a_{17} n(OH) + a_{26} n(NO)} \\ \times \left[ \frac{a_1 n(M) n(O_2)}{a_1 n(M) n(O_2) + a_2 n(O_3)} + \frac{a_6 n(O_3) + a_{30} n(H_2 O_2)}{a_5 n(O) + a_{36} n(CO)} \right] \quad (5)$$

A simplification of this expression leads to

$$\frac{n(HO_2)}{n(OH)} = \frac{a_5}{a_7} \frac{a_1 n(M) n(O_2)}{a_1 n(M) n(O_2) + a_2 n(O_3)} \approx \frac{a_5}{a_7} \quad (6)$$

in the upper stratosphere, to

$$\frac{n(HO_2)}{n(OH)} = \frac{a_6}{a_{6b}} \quad (7)$$

in the middle and lower stratosphere and to

$$\frac{n(HO_2)}{n(OH)} = \frac{a_{36} n(CO)}{a_{26} n(NO)} \quad (8)$$

below 15 km.

The global balance equation for  $\text{HO}_x = \text{H} + \text{OH} + \text{HO}_2$  is given by

$$\begin{aligned} & a^* n(\text{O}^1\text{D}) [n(\text{H}_2\text{O}) + n(\text{CH}_4) + n(\text{H}_2)] \\ & = a_{16} n^2(\text{OH}) + a_{17} n(\text{OH}) n(\text{HO}_2) + a_{38} n(\text{CH}_4) \\ & \quad n(\text{OH}). \end{aligned} \quad (9)$$

The distribution of hydroxyl and hydroperoxy radicals is determined assuming for water vapor, methane and molecular hydrogen a mixing ratio equal to 3, 1.5 and 0.5 ppmv respectively. These results are introduced in the ozone equation since the presence of hydrogen compounds introduces a supplementary loss rate given by

$$L_2(\text{O}_3) = \left\{ [a_5 n(\text{OH}) + a_7 n(\text{HO}_2)] \frac{J_3}{k_2 n(\text{M}) n(\text{O}_2)} \right.$$

$$+ a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6b} n(\text{HO}_2) \left. \right\} n(\text{O}_3) \quad (10)$$

or

$$L_2(\text{O}_3) = [a_2 n(\text{H}) + (a_5^e + a_6) n(\text{OH}) + (a_7^e + a_{6b}) n(\text{HO}_2)] n(\text{O}_3) \quad (11)$$

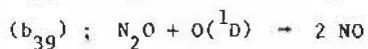
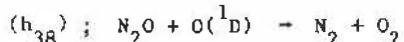
$$\text{if } a^e = \frac{a J_3}{k_2 n(\text{M}) n(\text{O}_2)} \quad (12)$$

In most part of the stratosphere, this expression can be simplified and the loss rate can be approximated by

$$L_2(\text{O}_3) = 2 (a_5^e + a_6) n(\text{OH}) n(\text{O}_3). \quad (13)$$

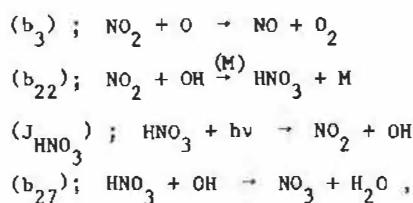
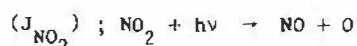
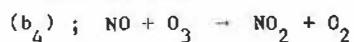
The effect of nitrogen compounds has also to be introduced. Stratospheric nitric oxide is formed by dissociation of nitrous oxide by the excited  $\text{O}^1\text{D}$  atom which is very reactive.

Reactions



have been proposed by Nicolet (1970) as an important production process for  $\text{NO}_x$ . Moreover, the reaction of nitrogen atoms with molecular oxygen can lead in less than 10 s in the lower stratosphere to nitric oxide molecules. These nitrogen atoms can be produced by cosmic rays whose intensity is related to the solar activity (Brasseur and Nicolet, 1973 ; Ruderman and Chamberlain, 1973).

In the ozonosphere, nitric oxide is partly converted into nitrogen dioxide. However, this molecule is rapidly dissociated by UV radiation or, above 35 km, by atomic oxygen. But, the presence of hydrogen compounds enhances all the  $\text{NO}_2$  molecules to reform NO since a fraction of them is converted into nitric acid by OH radicals. The  $\text{HNO}_3$  molecule can also be photodissociated by solar radiation or can be destroyed by hydroxyl radicals. Considering these most important reactions, namely



the ratios between the  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{HNO}_3$  concentration are

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_4 n(\text{O}_3)}{J_{\text{NO}_2} + b_3 n(\text{O})} \quad (14)$$

$$\frac{n(\text{HNO}_3)}{n(\text{NO}_2)} = \frac{b_{22} n(\text{OH})}{J_{\text{HNO}_3} + b_{27} n(\text{OH})} \quad (15)$$

The effect of nitrogen oxides on odd oxygen can be characterized by different catalytic cycles (Johnston, 1971). However, in the stratosphere, its influence on ozone can be summarized with a fairly good approximation by introducing an additional loss rate, namely

$$L_3(\text{O}_3) = 2 b_3^e n(\text{NO}_2) n(\text{O}_3) \quad (16)$$

$$\text{where } b_3^e = \frac{J_3}{k_2 n(\text{M}) n(\text{O}_2)}.$$

Finally, the global continuity equation for ozone can be written

$$\begin{aligned} & \frac{\partial n(\text{O}_3)}{\partial t} + \vec{\nabla} \cdot \vec{\phi} + [k_3^e n(\text{O}_3) + a_2 n(\text{H}) + (a_5^e + a_6) \\ & n(\text{OH}) + (a_7^e + a_{6b}) n(\text{HO}_2) + 2 b_3^e n(\text{NO}_2)] n(\text{O}_3) \\ & = 2 J_2 n(\text{O}_2). \end{aligned} \quad (17)$$

Table 1 Adopted rate constants\*

$k_2 = 1.1 \times 10^{-34} \exp(50/T) \text{ cm}^6 \text{ s}^{-1}$
$k_3 = 1.05 \times 10^{-11} \exp(-2169/T) \text{ cm}^3 \text{ s}^{-1}$
$a^* = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
$a_1 = 6.7 \times 10^{-33} \exp(290/T) \text{ cm}^6 \text{ s}^{-1}$
$a_2 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ s}^{-1}$
$a_5 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ s}^{-1}$
$a_6 = 1.3 \times 10^{-12} \exp(-950/T) \text{ cm}^3 \text{ s}^{-1}$
$a_{6h} = 3.3 \times 10^{-14} \exp(-1000/T) \text{ cm}^3 \text{ s}^{-1}$
$a_7 \approx a_5$
$a_{16} = 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
$a_{26} = 3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
$a_{30} = 4.1 \times 10^{-13} T^{1/2} e^{-600/T} \text{ cm}^3 \text{ s}^{-1}$
$a_{36} = 1.25 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
$a_{38} = 5 \times 10^{-12} e^{-1900/T} \text{ cm}^3 \text{ s}^{-1}$

\* References for these rate constants are given in the papers published at the Aeronomy Institute.

$$b_3 = 9.12 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

$$b_4 = 1 \times 10^{-12} \exp(-1250/T) \text{ cm}^3 \text{ s}^{-1}$$

$$b_{22} = 2 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$$

high pressure limiting coefficient :

$$5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

$$b_{27} = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$$

$$b_{38} = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

$$b_{39} = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

### 3. TRANSPORT

The mass transport in the stratosphere is due to advection (mean motion) and to eddy diffusion. In order to distinguish both processes, it can be considered that the total velocity of an atmospheric particle and its concentration can be divided into their mean value  $\langle v \rangle$  and  $\langle n \rangle$  and a fluctuation  $v'$  and  $n'$ . Thus

$$\vec{v} = \langle \vec{v} \rangle + \vec{v}' \quad (18)$$

and

$$n = \langle n \rangle + n' \quad (19)$$

The aleatory characteristic of  $\vec{v}'$  and  $n'$  is expressed by

$$\langle \vec{v}' \rangle = 0 \quad (20)$$

$$\text{and } \langle n' \rangle = 0. \quad (21)$$

The total particle flux can be written as

$$\vec{\phi} = \langle nv \rangle = \langle n \rangle \cdot \langle v \rangle + \langle n'v' \rangle \quad (22)$$

where the first term represents the contribution of the mean motion and the second term the effect of the turbulence.

The wind field can theoretically be determined by solving the equations of momentum, energy and continuity in the atmosphere. This problem has been considered by Cunnold et al (1974) who have presented a general circulation model of stratospheric ozone. In these preliminary results, the effect of the mean transport will not be taken into account but the dynamics will be parametrized by eddy diffusion only. The general circulation will be introduced in a later study, using observational data.

Eddy diffusion has been introduced for atmospheric studies by Lettau (1951) and Colegrove et al (1965) and has provided successful results in determining the composition of the upper atmosphere. This theory considers that a turbulent flux is created as soon as the density distribution of a trace gas is different from mixing conditions. Since the atmosphere cannot be considered as an isotropic medium and in order to introduce the possibility of a counter-gradient flux, we can use a general expression (Reed and German, 1965)

$$\tau_i = \langle n'v'_i \rangle = -n(M) \sum_j K_{ij} \frac{\partial f}{\partial x_j} \quad (i, j = 2, 3) \quad (23)$$

where  $f = n/n(M)$  is the volume mixing ratio and  $K_{ij} = K_{ji}$  represents the components of the eddy

diffusion tensor.

Values of  $K_{yy}$ ,  $K_{yz}$  and  $K_{zz}$  have been compiled by Reed and German (1965) at the altitudes of 16, 21 and 24 km and between the latitudes of 10°N and 80°N. Gudiksen et al (1968) have revised this work and extrapolated the values up to 27 km and down to 9 km. These data have been used to compute the dispersion of  $^{115}\text{W}$  injected in the tropical stratosphere during the summer of 1958 by nuclear explosions. Gudiksen's values of  $K_{yy}$  and  $K_{yz}$  are about 7-10 times lower than Reed and German's data.

Recently, Luther (1973) has performed a new analysis of the problem and has provided a table of data for the different seasons and the altitude range of 0 to 60 km. These values have been adopted by Widhopf and Taylor (1974) in their ozone model.

For these preliminary results, constant values of the eddy diffusion coefficients will be used, namely  $K_{yy} = 10^4 \text{ cm}^2 \text{ s}^{-1}$  and  $K_{yz} = 10^{10} \text{ cm}^2 \text{ s}^{-1}$ . In order to estimate the sensitivity of the latitudinal distribution of ozone to the counter-gradient flux, different values of  $K_{yz}$  will be considered.

### 4. MATHEMATICAL RESOLUTION

The steady state zonally averaged continuity equation which has to be solved, namely

$$\vec{\nabla} \cdot \vec{\phi} = P - L$$

where  $P$  and  $L = \beta n$  represent respectively the production and the loss rate of the studied constituent can be written in local coordinates ( $y, z$ ) by (see Bertin and Brasseur, 1974)

$$\left[ \frac{\partial}{\partial y} + \frac{\operatorname{tg} \lambda}{a} \right] \phi_y + \frac{\partial \phi_z}{\partial z} = P - L \quad (24)$$

if  $a$  is the Earth's radius,  $\lambda$  the geographical latitude,  $y$  and  $z$  the physical distances measured along respectively the meridians and the vertical of the Earth. Eliminating the two flux components with equation (23) the expression giving the volume mixing ratio  $f$  becomes

$$\begin{aligned} & K_{yy}^* \frac{\partial^2 f}{\partial y^2} + 2 K_{yz}^* \frac{\partial^2 f}{\partial y \partial z} + K_{zz}^* \frac{\partial^2 f}{\partial z^2} \\ & + \left[ \left( \frac{\partial}{\partial y} + \frac{\operatorname{tg} \lambda}{a} \right) K_{yy}^* + \frac{\partial K_{yz}^*}{\partial z} \right] \frac{\partial f}{\partial y} \\ & + \left[ \left( \frac{\partial}{\partial y} + \frac{\operatorname{tg} \lambda}{a} \right) K_{yz}^* + \frac{\partial K_{zz}^*}{\partial z} \right] \frac{\partial f}{\partial z} - \beta^* f = -P \quad (25) \end{aligned}$$

where

$$K_{ij}^* = K_{ij} / n(M)$$

$$\beta^* = \beta / n(M).$$

The problem has to be solved by a numerical method. At each point of a grid equation (25) is written in the form of a finite difference equation in which  $f(i,j)$  is related to the values of the 8 adjacent points by a linear

equation. This algebraic system is then solved using an alternating direction method. The iteration is performed until the difference between two successive solutions is less than 0.5%. The computation has been performed on an IBM 370-155 machine at the Aerospatiale in Paris.

## 5. RESULTS AND DISCUSSION

For these preliminary results, the meridional distribution of  $O_3$ ,  $O(^3P)$ ,  $O(^1D)$ , OH and  $HO_2$  is determined considering the reactions which have been introduced in section 2. The solar ultraviolet and visible flux and the  $O_2$  and  $O_3$  absorption cross sections are taken from the compilation of Ackerman (1971). The temperature structure is based on Murgatroyd's paper (1957). In this steady state model, the sun is located  $10^\circ$  from the equator in the summer hemisphere and the solar flux is adjusted in order to approximatively take into account the day and night effect. When the transport is included, boundary conditions have to be chosen. Because of a symmetry around the pole axe, a zero flux is imposed at  $\pm 90^\circ$  latitude. At the upper and lower boundaries (50 and 0 km) a fixed concentration is given. In the case of ozone, photochemical equilibrium values are adopted at the stratosopause and experimental data at the lower boundary.

### 5.1. Photochemical equilibrium distribution of ozone

We first calculate the ozone distribution assuming photochemical equilibrium conditions and including the effect of hydrogen and nitrogen compounds. The assumed  $NO_2$  vertical distribution is chosen according the observation (Ackerman and Muller, 1972) and is represented on figure 2 (curve 1). The results are shown on figure 3

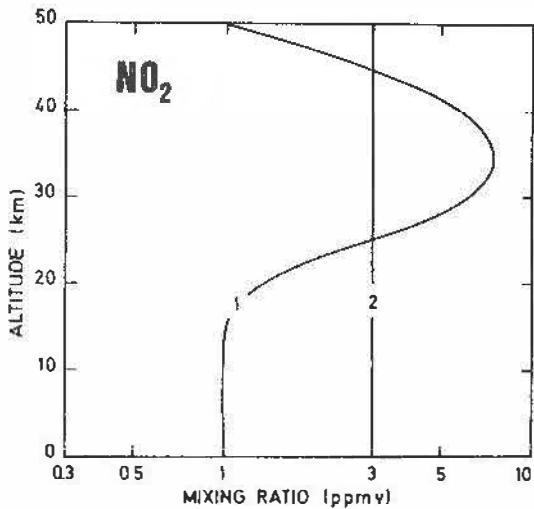


Fig. 2. Adopted vertical distribution of  $NO_2$  (curve 1).

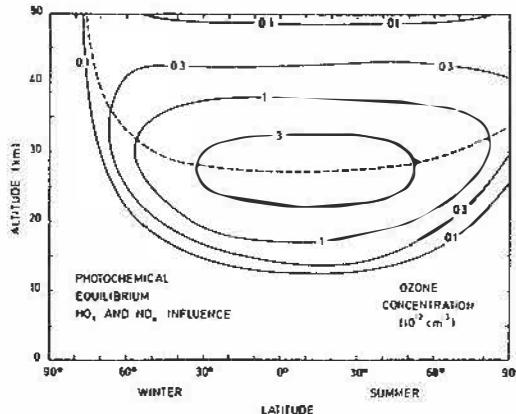


Fig. 3. Computed ozone distribution for photochemical conditions.

where it can be seen that a maximum of the ozone concentration appears around 27 km in the equatorial regions and at higher altitudes in the temperate and polar regions. At the stratosopause, the concentration is of the order of  $10^{11} \text{ cm}^{-3}$  at all latitudes except in the winter polar region where the dissociation of molecular oxygen is not possible. In the lower part of the stratosphere, the concentration sharply decreases. For example, at the equator, the concentration at 12 km is about ten times lower than the concentration at 17 km. Also, there is a rapid decrease of the concentration above  $60^\circ$  winter latitude. At 30 km, there is a variation of a factor of 10 between  $60^\circ$  and  $70^\circ$  (winter).

### 5.2. Effect of transport

If the results previously discussed (figure 3) are compared with the observation (figure 4), major differences clearly appear.

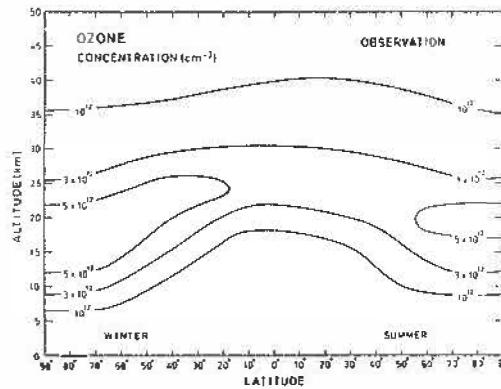


Fig. 4. Mean values of the observed ozone concentration (after London).

On the one hand, experimental data show the presence of a large amount of ozone in the lower stratosphere and in the troposphere. A value of  $5 \times 10^{11} \text{ cm}^{-3}$  for the concentration at ground level is not an unreasonable value. On the other hand, the ozone quantity in the polar regions is larger than in the tropical and equatorial zones. Since the production of ozone mainly occurs in the most U.V. irradiated regions, the presence

of ozone at high latitudes, especially in the winter hemisphere has to be explained by the atmospheric dynamics. As an example of the relative importance of each eddy diffusion coefficient ( $K_{zz}$ ,  $K_{yy}$  and  $K_{yz}$ ), the vertical distribution of ozone is established in different cases on figure 5.

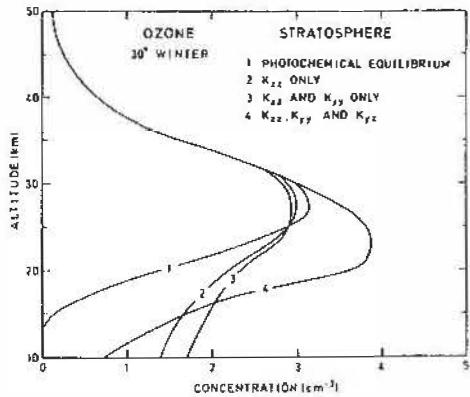


Fig. 5. Examples of the vertical distribution of ozone for different transport conditions.

Curve 1 shows the obtained profile if only the chemistry (including  $\text{HO}_x$  and  $\text{NO}_x$ ) is taken into account. The introduction of vertical transport (curve 2) slightly reduces the concentration at the maximum but increases its value below 25 km. The effect of  $K_{yy}$  is not very important in the middle latitudes but it plays a larger role in the high latitudes. The introduction of a counter gradient flux ( $K_{yz}$ ) increases the concentration above the tropopause and lowers the altitude of the concentration maximum. The effect of  $K_{yy}$  and  $K_{zz}$  is also seen on figure 6 which has to be compared with figure 3 and 4. The

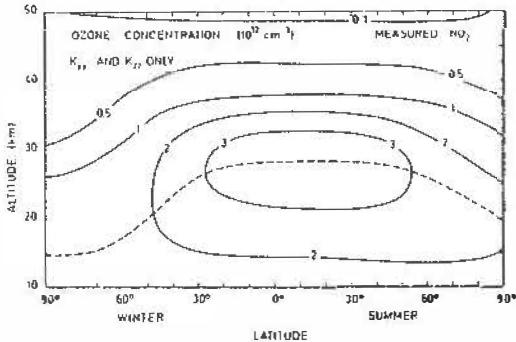


Fig. 6. Computed ozone distribution when  $K_{yz}$  is neglected. The  $\text{HO}_x$  and  $\text{NO}_x$  chemistry is included.

existence of a horizontal flux ( $K_{yy}$ ) increases the ozone concentration in the polar region but this quantity remains larger near the equator and in the tropics. Such a result has been obtained by Jessen (1973) and also by Shimazaki et al (1973) when the winds were neglected.

The introduction of the anisotropic component  $K_{yz}$  entirely modifies the latitudinal distribution of ozone. Adopting for  $|K_{yz}|$  a value somewhat larger than  $10^7 \text{ cm}^2 \text{ s}^{-1}$  in the winter

hemisphere and equal to  $8 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$  in the summer hemisphere the obtained ozone chart (figure 7) is close to the observed values

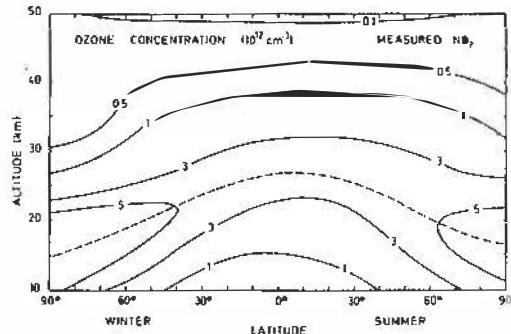


Fig. 7. Computed ozone chart. The  $\text{HO}_x$  and  $\text{NO}_x$  chemistry is included. The transport is parametrized by the three components of the eddy diffusion tensor.

(figure 4). The concentration now appears to be higher in the polar regions and the height of this maximum decreases from 27 km at the equator to 17 km in the summer polar region and to 15 km in the winter polar region. Whatever the adopted transport process is, the distribution of ozone above 30 km remains the same, which confirms the fact that photochemical conditions can be accepted in the upper stratosphere.

The effect of the dynamics on total ozone is shown on figure 8. As expected larger ozone

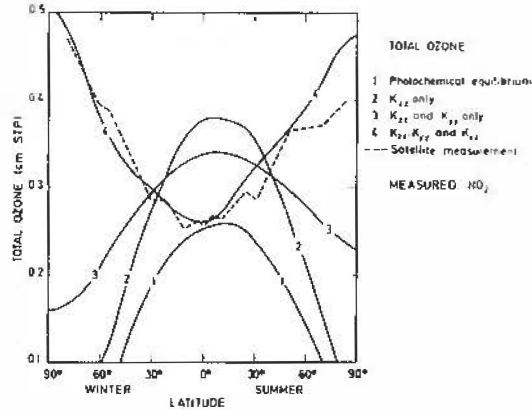


Fig. 8. Ozone column for different transport conditions and comparison with satellite data. The importance of  $K_{yz}$  is shown.

values near the poles are obtained only if a sufficiently high value of  $K_{yz}$  is introduced. The effect of vertical transport only leads to an increase of the ozone content due to the presence of the  $\text{O}_3$  molecule in the lower stratosphere and troposphere. The adopted value for  $|K_{yz}|$  is very crucial as shown on figure 9 where three different constant values, namely  $10^6$ ,  $5 \times 10^6$  and  $10^7 \text{ cm}^2 \text{ s}^{-1}$ , are adopted. At  $75^\circ$  winter, for example, the ozone content is given by respectively 0.25, 0.35 and 0.45 cm STP.

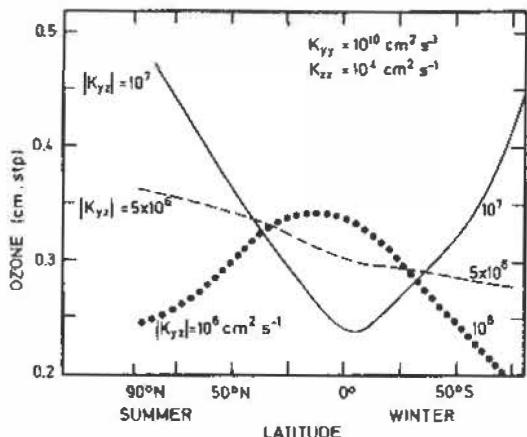


Fig. 9. Ozone column for three different values of the anisotropic component  $|K_{yz}|$

In order to estimate with greater precision the atmospheric regions characterized by detached ozone, the production, the loss and the transport rate have been represented on figure 10, 11 and 12 when the model of figure 7 is adopted. The production and the loss rate maxima

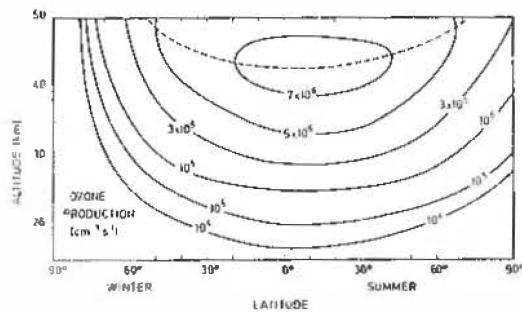


Fig. 10. Meridional distribution of the ozone production in the stratosphere.

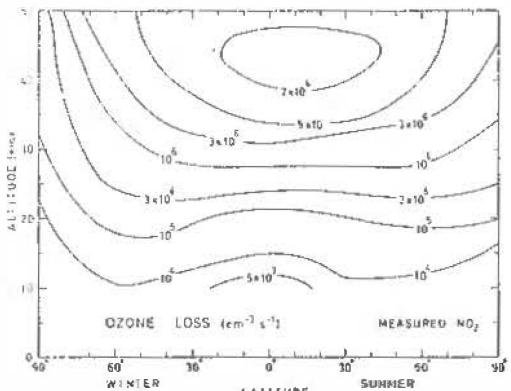


Fig. 11. Meridional distribution of the ozone loss.

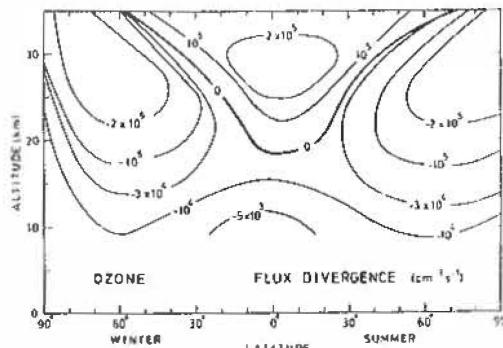


Fig. 12. Meridional distribution of the flux divergence of ozone. The regions of detached ozone can be seen.

appear to be around 45 km height in the equatorial regions, thus higher than the ozone concentration maximum. Since, photochemical conditions can be accepted above 30-35 km, the distribution of the production and the loss rate ( $P$  and  $L$ ) are almost identical in the upper stratosphere ( $P=L$ ). However, in the lower stratosphere, the flux divergence has the same order of magnitude as  $P$  and  $L$  and at the tropopause, there is an equilibrium between the transport and the loss rate ( $\nabla \cdot \vec{A} = -L$ ). Figure 12 clearly shows these features and also represents the atmospheric regions with dominant production and loss rates.

### 5.3. Effect of the chemistry

Using the transport data which provide an ozone distribution close to the observation, some sensitivity studies have been done and the distribution of some other minor constituents has been undertaken.

First, the ozone distribution is computed considering a pure oxygen atmosphere only. The shape of the latitudinal distribution remains the same but higher values of the concentration are obtained. For example, around 20 km the concentration becomes larger than  $10^{13} \text{ cm}^{-3}$  above  $80^\circ$ . At the equator, the concentration is about 1.5 larger than if the effect of  $\text{NO}_x$  is considered. Globally, the introduction of the hydrogen and nitrogen compounds effect reduces the ozone quantity by about 33%. Figure 13 shows the effect of  $\text{HO}_x$  and  $\text{NO}_x$  at  $45^\circ$  winter and the observation by Hering and Borden is also represented.

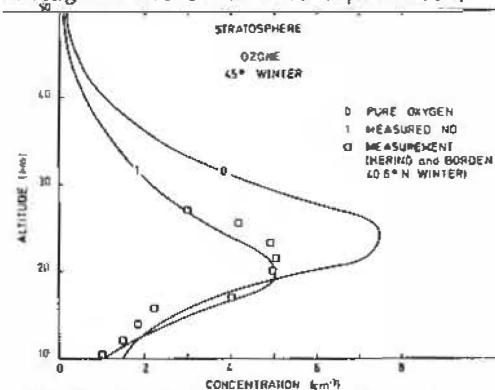


Fig. 13. Vertical distribution of ozone computed in a pure oxygen atmosphere and when the effect of  $\text{NO}_x$  is included. The results at  $45^\circ$  winter are compared with the measurement of Hering and Borden at  $40.6^\circ\text{N}$ .

The distribution of atomic oxygen in its electronic states  $^3P$  and  $^1D$  are given on figure 14 and 15. The  $O(^1D)$  atom plays an important role

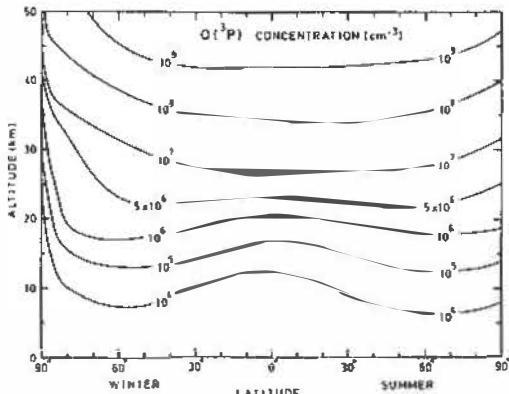


Fig. 14. Meridional distribution of the  $O(^3P)$  atom.

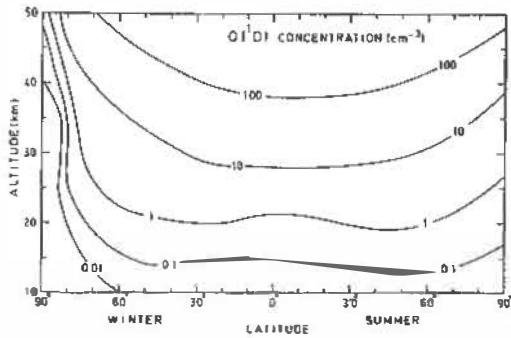


Fig. 15. Meridional distribution of the  $O(^1D)$  atom.

in the stratospheric chemistry since it dissociates methane, water vapor, molecular hydrogen and nitrous oxide.

The distribution of hydrogen compounds has also been computed as well as the ratio between the concentrations of  $HO_2$  and OH. If  $a_7$  is chosen to be equal to  $a_5$ , this ratio is of the order of 1 at the stratopause. But below 40 km, where reactions  $a_6$  and  $a_{6b}$  become dominant, the ratio increases to reach about 50 at the tropopause. It should be noted that  $n(HO_2)/n(OH)$  is almost independent from the latitude (figure 16). The concentration of the hydroxyl radicals does not vary by more than a factor of 10 between 20 and 45 km except in the winter polar regions where the solar radiation does not penetrate. Figure 17 shows that the OH concen-

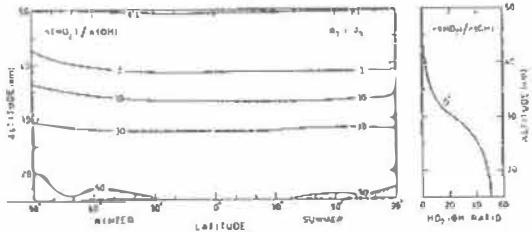


Fig. 16. Ratio of the  $HO_2$  to OH concentration.

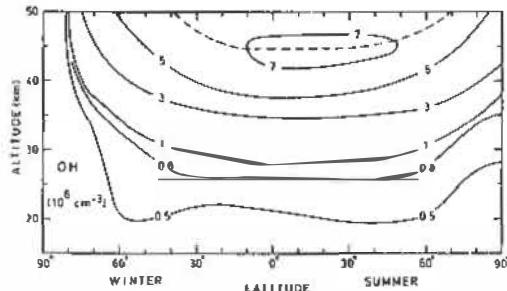


Fig. 17. Meridional distribution of the hydroxyl radical in the stratosphere.

tration maximum appears in the region where the ozone production is the largest. On the other hand, the maximum of the  $HO_2$  concentration (figure 18) is found around 27 km in the equatorial regions.

The latitudinal variation of the hydrogen compounds is of importance since the OH radical leads to the formation of nitric acid.

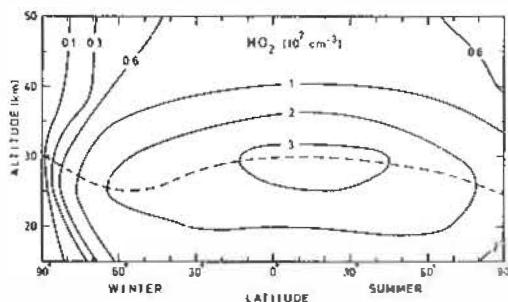


Fig. 18. Meridional distribution of the hydroxyl radical in the stratosphere.

## 6. SUMMARY

This model, in its preliminary form, has provided a theoretically determined ozone distribution in the meridional plane which is in good agreement with observational data. The sensitivity of the chemistry is important and, even in a simplified scheme, it can be seen that the three components of the eddy diffusion tensor play a particular role. The distribution of  $O(^3P)$ ,  $O(^1D)$ , OH and  $HO_2$  which play a leading role in the aeronomical behavior of the stratosphere have also been determined. Further developments of the model should include the effect of the general circulation and should lead to the determination of nitrogen or carbon compounds below 50 km.

## 7. ACKNOWLEDGMENTS

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