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Aeronomic chemistry of the stratosphere

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FOREWORD

"Aeronomic Chemistry of the Stratosphere" is an invited paper at the Survey Conference on Climatic Impact Assessment Program of the United States Department of Transportation, Cambridge, Massachusetts, February 15 and 16, 1972. It will be published in the Conference Proceedings and Planetary and Space Science.

AVANT-PROPOS

"Aeronomic Chemistry of the Stratosphere" a été présenté à Cambridge, Massachusetts en février 1972, à la Survey Conference on Climatic Assessment Program of the United States Department of Transportation. Ce texte paraîtra également dans les Proceedings de la Conférence et dans Planetary and Space Science.

VOORWOORD

"Aeronomic Chemistry of the Stratosphere" werd voorgedragen tijdens The Survey Conference on Climatic Impact Assessment Program of the United States Department of Transportation, welke plaats had te Cambridge, Massachusetts, in februari 1972. Deze tekst zal ook gepubliceerd worden in de Proceedings van de vergadering en in Planetary and Space Science.

VORWORT

"Aeronomic Chemistry of the Stratosphere" wurde in Cambridge, Massachusetts, in Februar 1972, zu der "Survey Conference on Climatic Assessment Program of the U.S. Department of Transportation", vorgetragen. Dieser Text wird in die Proceedings dieser Konferenz und in Planetary and Space Science, herausgegeben.

AERONOMIC CHEMISTRY OF THE STRATOSPHERE

by

Marcel NICOLET

Abstract

In the stratosphere, dissociation of H_2O, CH_4 and H_2O is brought about, mainly, by reaction processes with excited oxygen atoms produced by the photodissociation of ozone. A discrepancy noted between theoretical and observational concentrations of O_3 in the upper stratosphere suggests two possible explanations : solar radiation fluxes for O_2 photodissociation which are too large along with too large rate coefficients and absorption cross sections or ozone reduction brought about by the effect of hydrogen compounds or of nitrogen oxides.

The reaction of the excited oxygen atom with methane and nitrous oxide leads to a destruction of these two molecules in the stratosphere which corresponds to a production of carbon monoxide with water vapor and of nitric oxide, respectively. The vertical distribution of water vapor is not affected by its dissociation in the stratosphere since its re-formation is rapid.

The fact that the ratio of the hydroxyl and hydroperoxyl radical concentrations cannot be determined with adequate precision complicates the calculation of the destruction of ozone which occurs through reactions of OH and HO_2 not only with atomic oxygen in the upper stratosphere but also with CO and NO in the lower stratosphere, respectively. The same difficulty arises in connection with the dissociation of nitric acid molecules formed by the reaction of OH and NO_2 ; destruction processes by photodissociation or by reaction with OH are not yet known with precision. Another difficulty, of a different kind, is that the nitric oxide concentration is not well known at the stratopause level.

Résumé

La dissociation de la vapeur d'eau, du méthane et de l'hydrogène moléculaire dans la stratosphère est due à la réaction de l'atome d'oxygène dans son premier état excité qui est produit au cours de la photodissociation de l'ozone.

La différence que l'on constate entre les valeurs de la concentration de l'ozone observée dans la haute stratosphère et celles qui sont déterminées théoriquement suggère deux types d'explications possibles. La photodissociation de l'oxygène est trop élevée par suite d'une surestimation des coefficients de réaction ou (et) du rayonnement solaire ou (et) des coefficients d'absorption ; ou bien la réduction de l'ozone peut provenir d'effets des composés de l'hydrogène ou des oxydes d'azote.

La réaction de l'atome excité d'oxygène avec CH_4 et N_2O conduit à une destruction de ces deux molécules dans la stratosphère qui correspond respectivement à une production du monoxide de carbone CO et de la vapeur d'eau H_2O et à celle de l'oxyde d'azote NO. D'autre part, la dissociation de la vapeur d'eau par le même processus n'influence pas sa distribution dans la majeure partie de la stratosphère par suite de sa reformation très rapide.

Le calcul de la destruction de l'ozone par les composés hydrogénés est compliqué par suite de la difficulté de déterminer avec suffisamment de précision (coefficients de réaction trop imprécis) le rapport des radicaux OH et HO_2 dépendant de la concentration de l'atome d'oxygène dans la stratosphère supérieure et de NO avec CO dans la stratosphère inférieure. Un type analogue de difficulté se présente en relation avec la dissociation de HNO_3 par des processus différents comme sa réaction avec OH ou la photodissociation directe. Enfin, tant que l'on ne connaît pas la concentration de NO à la stratopause on se heurte à un autre type de difficulté empêchant le calcul exact de l'effet des oxydes d'azote sur la concentration de l'ozone.

Samenvatting

De dissociatie van H_2O, CH_4 en H_2 in de stratosfeer is te wijten aan de reacties met geëxciteerde atomaire zuurstof die geproduceerd wordt door fotodissociatie van ozon.

Het verschil dat men merkt tussen de concentratie van ozon waargenomen in de hogere atmosfeer en de theoretische berekende waarde suggereert twee mogelijke verklaringen : de fotodissociatie van zuurstof is te groot tengevolge van een overschatting der reactiecoëfficiënten, of (en) van de zonnestraling, of (en) van de absorptiecoëfficiënten ; ofwel kan de vermindering van ozon het gevolg zijn van de werking van waterstofverbindingen of van de stikstofoxydes.

De reactie van geëxciteerde atomaire zuurstof met methaan en N_2O leidt tot een vernietiging van deze twee molekulen in de stratosfeer en correspondeert respectievelijk met de productie van CO en waterdamp H_2O, en stikstofoxyde NO. De dissociatie van waterdamp in de stratosfeer heeft geen invloed op de vertikale distributie van H_2O aangezien deze molekule zeer vlug gevormd wordt.

Het feit dat de verhouding van de concentraties der hydroxyl en hydroperoxyl radicalen niet bepaald kunnen worden met voldoende nauwkeurigheid, bemoeilijkt de berekening van de vernietiging van ozon die te wijten is aan reacties van OH en HO_2 met atomaire zuurstof in de hogere stratosfeer en met CO en NO in de lagere atmosfeer. Een gelijkaardige moeilijkheid doet zich voor in verband met de dissociatie van HNO_3 gevormd door de reactie van OH en NO_2 ; vernietiging door fotodissociatie of door reactie met OH zijn nog niet met voldoende gekend. Zolang de concentratie van NO aan de stratopause niet gekend is, stoot men op moeilijkheden die niet toelaten nauwkeurige berekeningen te maken betreffende de invloed van stikstofoxydes op de concentratie van ozon.

Zusammenfassung

Die Zerstörung des H_2O, CH_4 und H_2 in der Stratosphäre, ist durch die Reaktion der Sauerstoffatome die von der Ozonphotodissoziation entstehen, gefordert.

Der Unterschied zwischen die gemessene und theoretische Ozondichte, kann von zwei verschiedene Ursachen vorkommen : entweder ist die Photodissoziation des Sauerstoffes überschätzt wegen eine Überschätzung der Reaktionkoeffiziente, oder (und) der Intensität der Sonnenstrahlung, oder (und) der Absorptionkoeffizienten ; Oder ist diese Ozondichte reduziert durch Auswirkungen der verschiedenen zusammengefesster Wasserstoffmolekulen oder der Stickstoffoxyden.

Die Reaktion der angeregten Sauerstoffatome mit CH_4 und H_2O fordert die Zerstörung dieser Molekulen in der Stratosphäre, und produziert CO und H_2O so wie NO. Die Dissoziation des H_2O beinflüsst aber nicht die Dichteverteilung dieser Molekulen in der Stratosphäre, wegen seiner kurzen Zusammenstellungszeit.

Die Berechnung der Zerstörungsgeschwindigkeit des O_3 durch die Wasserstoff Reaktionen ist sehr kompliziert denn das Dichteverhältniss des OH und HO_2 ist nicht genau gekannt. Die selben Schwierigkeiten findet man im Falle der Dissoziation des HNO_3. So lange die Dichte des NO an der Stratopausehöhe nicht gekannt ist, ist es nicht möglich eine genaue Berechnung der Wirkung der Stickstoffoxyden auf die Ozondichteverteilung zu geben.

I. INTRODUCTION

Theories of the ozone distribution in the terrestrial atmosphere have been given by Chapman (1930,1943). He first considered the balance between the formation and destruction of ozone in relation to its regular daily and annual variations. The atmosphere was considered as static without horizontal or vertical transfer of ozone. Any reactions with nitrogen or other atmospheric constituents were ignored.

The introduction of hydrogen compounds in the photochemical treatment of the ozone problem by Bates and Nicolet (1950) led to the first indication of a possible action of hydroxyl and hydroperoxyl radicals on the ozone distribution, especially in the mesosphere where the photodissociation of water vapor and methane occur. Furthermore, in the stratosphere, the reaction of H_2O with the electronically excited atomic oxygen in the ^1D state (Cadle, 1964 ; Hampson, 1964) leads to the possibility of its dissociation in the stratosphere. The concentrations of $O(^1D)$ produced by ozone photolysis in the stratosphere and troposphere are sufficiently large to lead to OH radicals (and H atoms) not only from water vapor but also from methane and molecular hydrogen. Finally, the action of nitrogen oxides on ozone (Crutzen, 1970 ; Johnston, 1971) may be considered in the atmospheric ozone equilibrium. However, the formation of nitric acid (Nicolet, 1965, 1970b ; Johnston, 1971) seems to be the mechanism responsible for the removal of nitrogen oxides.

II. THE OZONE FORMATION

The equations governing the rates of change of the concentration of ozone and atomic oxygen, $n(O_3)$ and $n(O)$ are

$$\frac{dn(O)}{dt} + 2\ k_1\ n(M)\ n^2(O) + k_2\ n(M)\ n(O_2)\ n(O) + k_3\ n(O_3)\ n(O)$$

$$= 2n(O_2)\ J_2 + n(O_3)\ J_3 \qquad (1)$$

and

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

which lead to the general form

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1\ n(M)\ n^2(O) + 2k_3\ n(O_3)\ n(O)$$

$$= 2\ n(O_2)\ J_2\ . \qquad (3)$$

In these equations, J_2 and J_3 are the photodissociation coefficients of O_2 and O_3, respectively,

$$(J_2)\ ;\ O_2 + h\nu \rightarrow O + O \qquad (4)$$

$$(J_3)\ ;\ O_3 + h\nu \rightarrow O_2 + O\ . \qquad (5)$$

The rate coefficients are

$$(k_1)\ ;\ O + O + M \rightarrow O_2 + M \qquad (6)$$

$$(k_2)\ ;\ O + O_2 + M \rightarrow O_3 + M \qquad (7)$$

$$(k_3)\ ;\ O + O_3 \rightarrow 2\ O_2\ . \qquad (8)$$

In the stratosphere, reaction (6) takes place very slowly and can be omited in all photochemical discussions of stratospheric ozone (Bates and Nicolet,1950).

Furthermore, atomic oxygen is always in photochemical equilibrium with ozone. Therefore, the rate of change of $n(O_3)$ in the stratosphere becomes.

$$\frac{dn(O_3)}{dt} + \frac{2k_3\ J_3}{k_2\ n(M)\ n(O_2)}\ n^2(O_3) = 2n(O_2)\ J_2\ . \tag{9}$$

Introducing the time $\tau_q(O_3)$, necessary to attain 50 % of the photochemical value $n_*(O_3)$, the following equation is obtained

$$\tau_{eq}(O_3) = 0.275\ n_*(O_3)/n(O_2)\ J_2\ . \tag{10}$$

With numerical values (Table I), it can be shown (see Fig. 5a) that photochemical equilibrium can be adopted for $n(O_3)$ at the stratopause. From (9), the following equation

$$n_*^2\ (O_3) = \frac{k_2}{k_3}\ n(M)\ n^2(O_2)\ \frac{J_2}{J_3} \tag{11}$$

represents photochemical equilibrium conditions in the stratosphere for a pure oxygen atmosphere. The numerical values of the ozone concentration $n(O_3)$ depend on the ratios k_2/k_3 and J_2/J_3.

The ratio k_2/k_3 is not yet known with sufficient accuracy for aeronomic purposes. According to Clyne et al. (1965) the following expression for k_2 represents their experimental data over the temperature range 188-373°K, (if $M = N_2, O_2$),

$$k_2 = 3.7 \times 10^{-35}\ e^{900/T}\ cm^6\ sec^{-1}\ . \tag{12a}$$

From Kaufman and Kelso (1967) the result is

$$k_2(N_2, O_2) = (5.8 \pm 1.0) \times 10^{-34}\ cm^6\ sec^{-1} \tag{12b}$$

TABLE I.- Atmospheric parameters in the stratosphere

Altitude (km)	Temperature (°K)	Total concentration (cm^{-3})	Ozone (Example) (cm^{-3})
15	211	3.9×10^{18}	1.0×10^{12}
20	219	1.7×10^{18}	2.9×10^{12}
25	227	7.7×10^{17}	3.2×10^{12}
30	235	3.6×10^{17}	2.9×10^{12}
35	252	1.7×10^{17}	2.0×10^{12}
40	268	8.1×10^{16}	1.0×10^{12}
45	274	4.3×10^{16}	3.2×10^{11}
50	274	2.3×10^{16}	1.0×10^{11}

for T = 300 °K. Other measurements (Hochanadel et al. 1968 ; Mulcahy and Williams, 1968 ; Donovan et al. 1970) lead to various values of the same order of magnitude, indicating differences of about a factor of two over the temperature range 200 to 300 °K. The value recommended by Johnston (1968) is (see Fig. 1a)

$$k_2(N_2, O_2) = 1.85 \times 10^{-35} \, e^{1050/T} \, \mathrm{cm}^6 \, \mathrm{sec}^{-1} \, , \qquad 12c)$$

while a recent measurement by Davis (1972) between 200 °K and 346 °K leads to (see Fig. 1a)

$$k_2(N_2) = (1.1 \pm 0.7) \times 10^{-34} \, e^{+(500 \pm 50)/T} \, \mathrm{cm}^6 \, \mathrm{sec}^{-1} \qquad (12d)$$

A comparison made between (12a), (12b), (12c) and (12d) is illustrated in Fig. 1a over the temperature range 150 °K - 300 °K. It shows that there is a difference of about a factor of 2 at 225 °K, reaching a factor of 4 near 160 °K. At 300 °K there is good agreement between the various measurements (cf Kaufman's and Kelso's data).

As far as the rate coefficient k_3 is concerned the value recommended by Johnston (1968) is

$$k_3 = 2 \times 10^{-11} \, e^{-2395/T} \, \mathrm{cm}^3 \, \mathrm{sec}^{-1} \qquad (13a)$$

Recent measurements over the temperature range 200 to 300 °K by Krezenski, Simonaitis and Heicklen (1971) leads to

$$k_3 = (1.1 \pm 0.2) \times 10^{-11} \, e^{-(2150 \pm 100)/T} \, \mathrm{cm}^3 \, \mathrm{sec}^{-1} \qquad (13b)$$

and over the temperature range 269 to 409 °K by McCrumb and Kaufman(1971) leads to

$$k_3 = (1.78 \pm 0.28) \times 10^{-11} \, e^{-(2230 \pm 50)/T} \, \mathrm{cm}^3 \, \mathrm{sec}^{-1} \, . \qquad (13c)$$

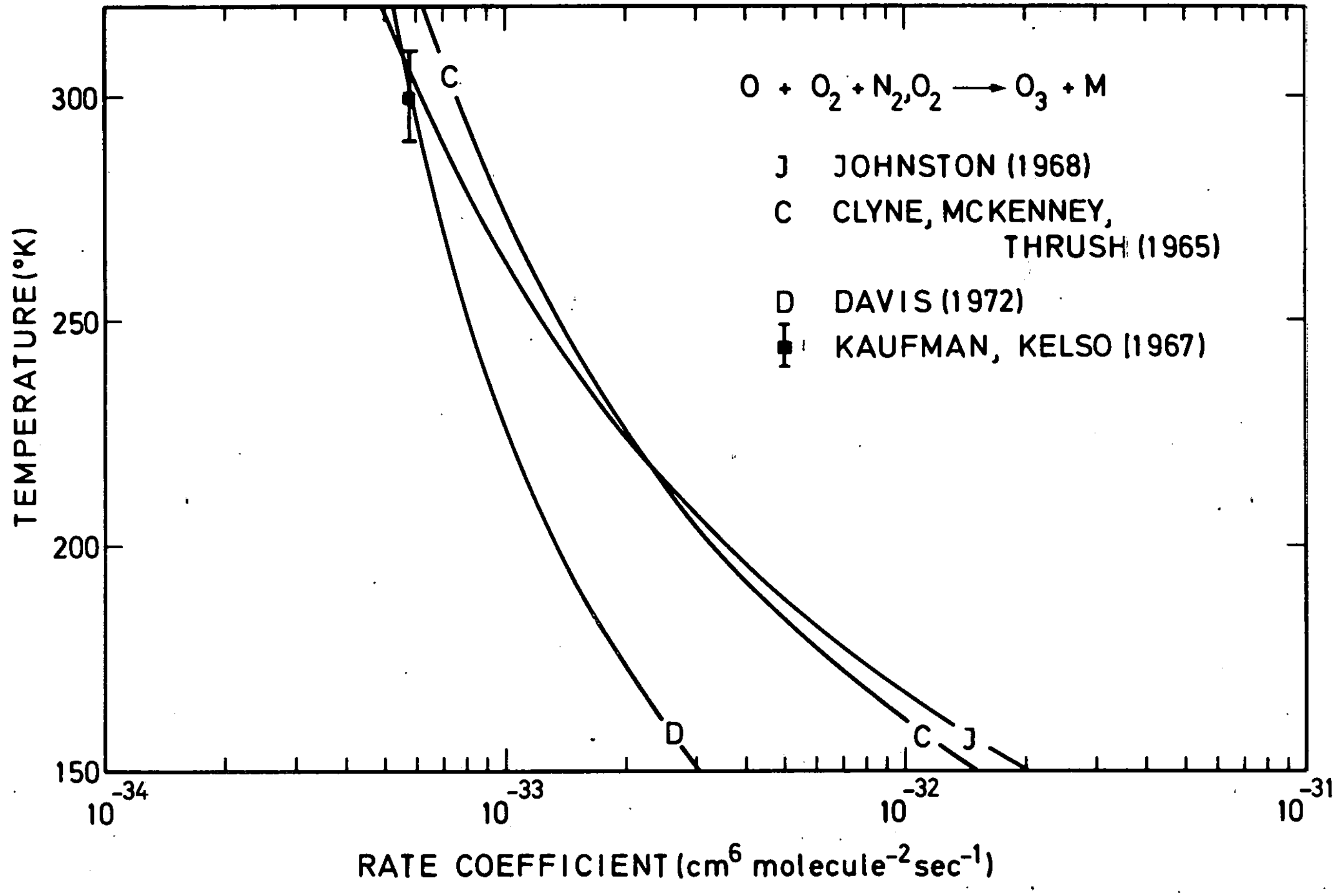

Fig. 1a.- Experimental values of the rate coefficient k_2 (cm^6 sec^{-1}) of the three body reaction $O_2 + O + M \rightarrow O_3 + M$ when the third body is N_2(4/5) and O_2(1/5).

Expressions (13b) and (13c) lead to the same numerical values below 200 °K where the difference with (13a) is about a factor of 2 (see Fig. 1b).

Therefore, using (12d) with (13b) and (12c) with (13a), the ratio k_2/k_3 which plays an important role in equation (11) can be written,

$$\frac{k_2(\text{Davis})}{k_3(\text{Heicklen})} = (1.0 \pm 0.2) \times 10^{-23}\ e^{(2650 \pm 250)/T}\ \text{cm}^3 \qquad (14a)$$

and

$$\frac{k_2(\text{Johnston})}{k_3(\text{Johnston})} = 9.26 \times 10^{-25}\ e^{3445/T}\ \text{cm}^3\ , \qquad (14b)$$

respectively. Differences of a factor of about 5 and of about 2 occur at 200 °K and 270 °K, respectively, as it is shown in Fig. 1c. A special and careful analysis of the ratio k_2/k_3 over the temperature range 150 - 300 °K is required for the analysis of aeronomic processes in the stratosphere and mesosphere.

As far as the photodissociation coefficients are concerned, it seems that new observations of the solar radiation are needed in the 2300 - 2000 A spectral range where O_2 is photodissociated. The photodissociation coefficients J_2, which are given in Fig. 2, depend on the ultraviolet solar flux data (Fig. 3) deduced by Ackerman et al.(1971). Using the data tabulated by Ackerman (1971) and a ratio k_2/k_3 equivalent to formula (14b) (Nicolet,1970), the results obtained are shown in Fig. 4 indicating that the theoretical values of the ozone concentrations are greater than the observational values (Krueger, 1969 ; Hilsenrath, 1969 and 1971 ; Randhava, 1971) above 30 km.

It is clear that it is possible to decrease the theoretical value $n_*(O_3)$ if the recent ratio k_2/k_3 obtained from (14a) is used instead of the ratio (14b). Furthermore, two other additional factors must be considered :

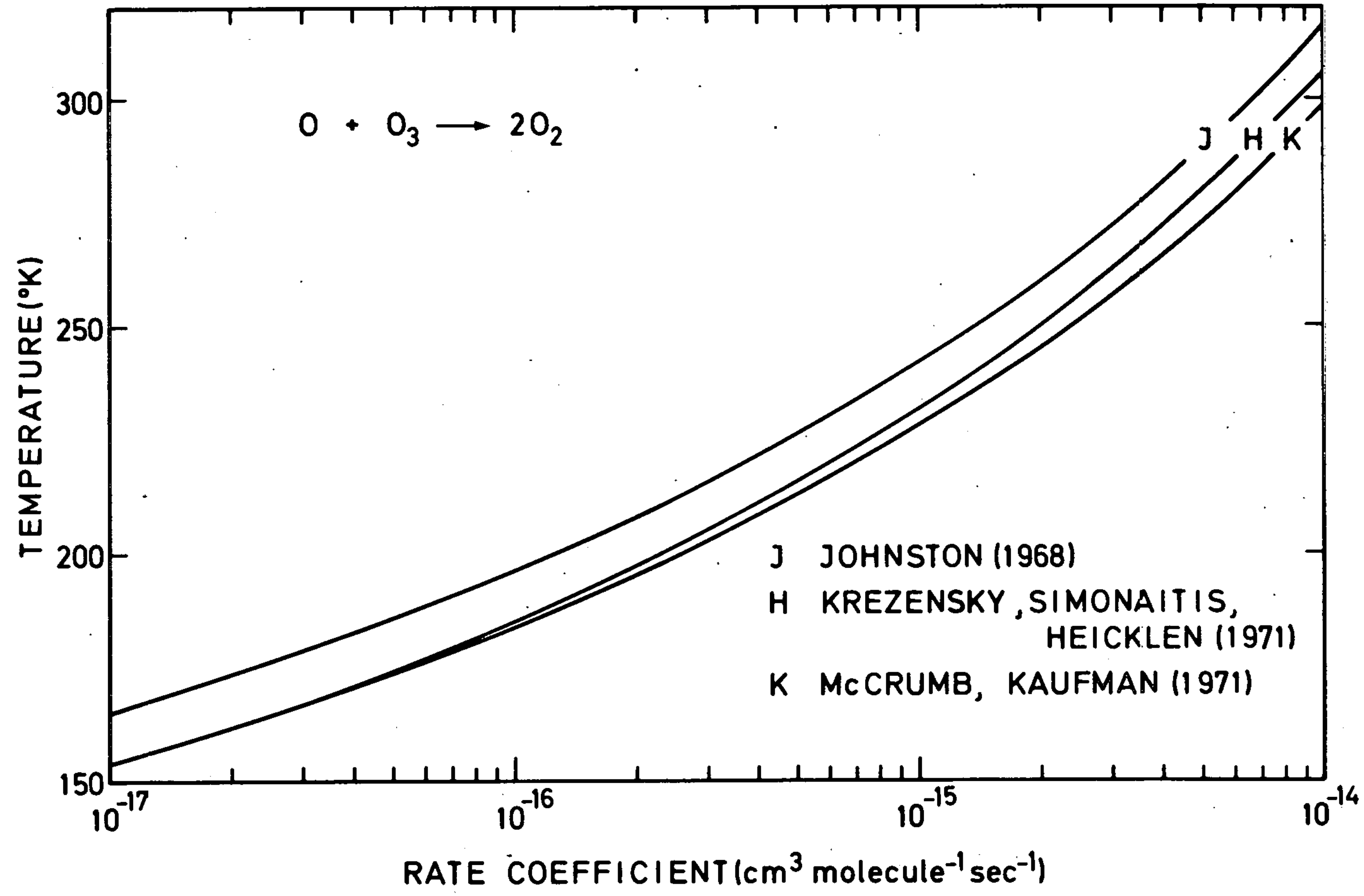

Fig. 1b.- Experimental values of the rate coefficient k_3 (cm^3 sec^{-1}) of the reactions $O + O_3 \rightarrow 2\ O_2$.

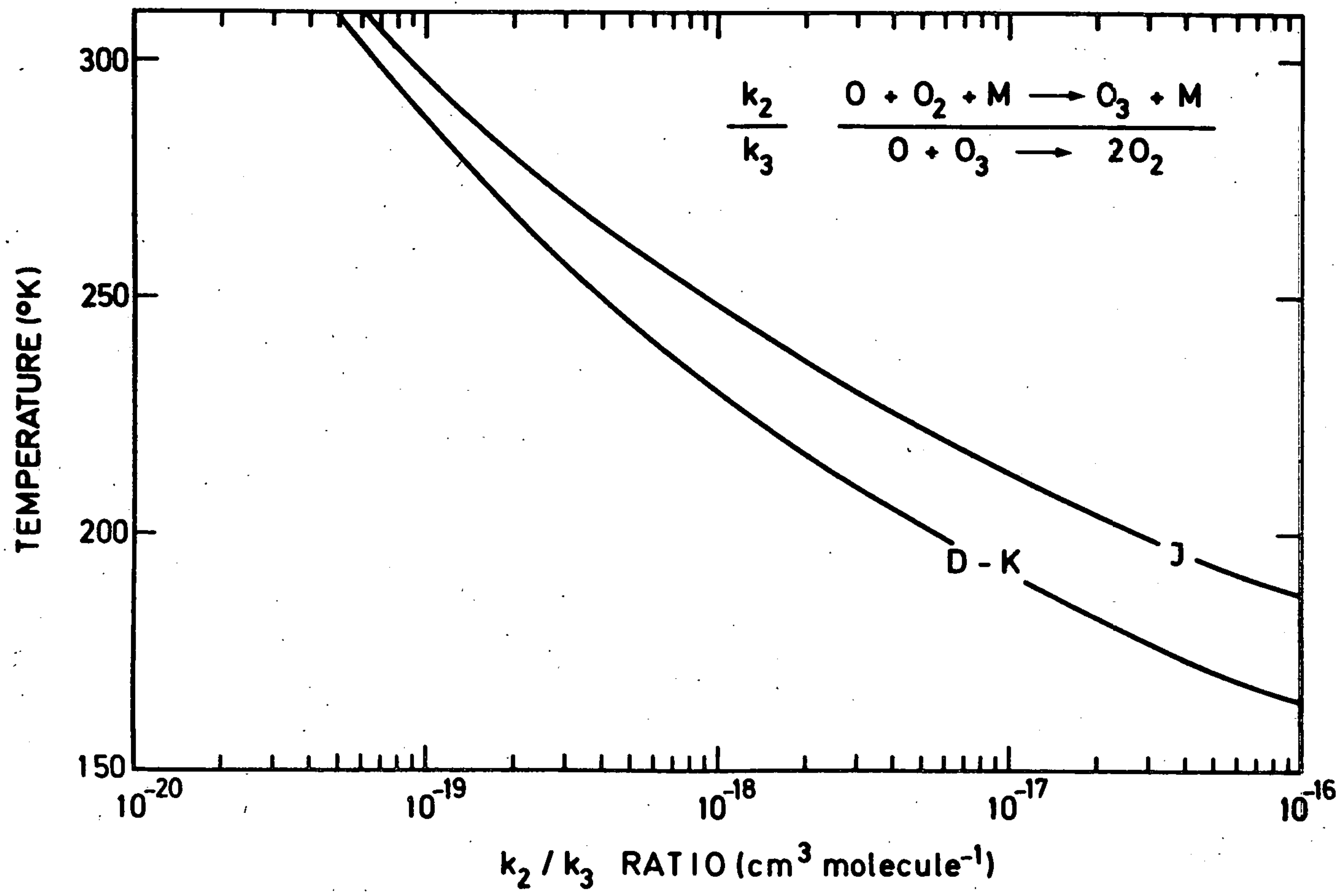

Fig. 1c.- Experimental values of the ratios of the rate coefficient k_2 and k_3 given in fig. 1a and fig. 1b.

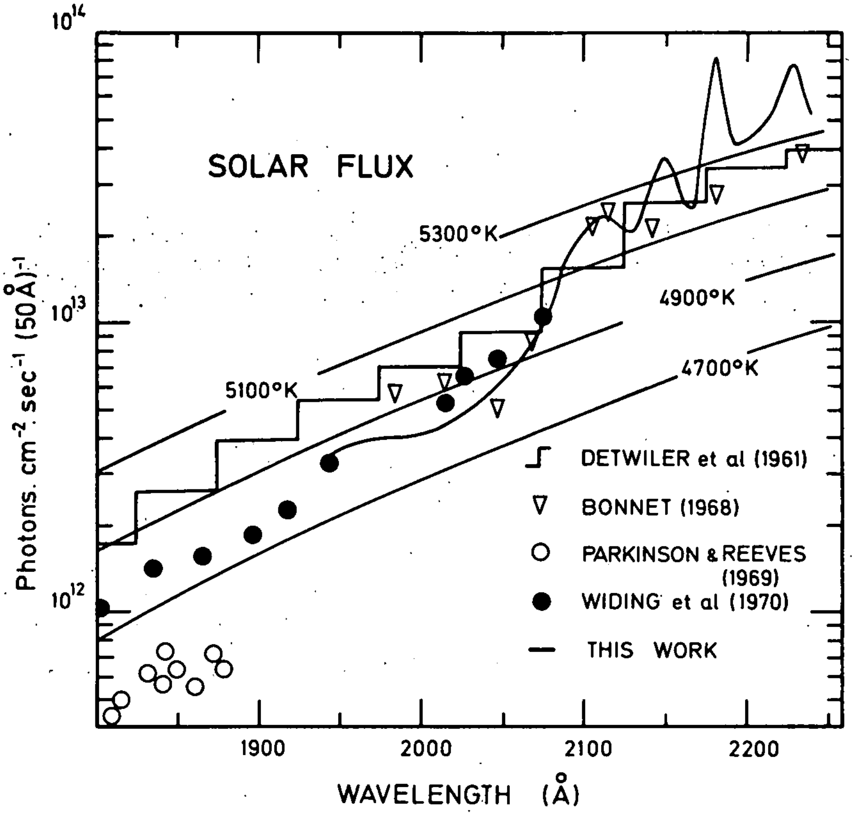

Fig. 2.- Observational data of solar radiation in the 1800-2250 A spectral range according to Ackerman, Frimout and Pastiels (1971).

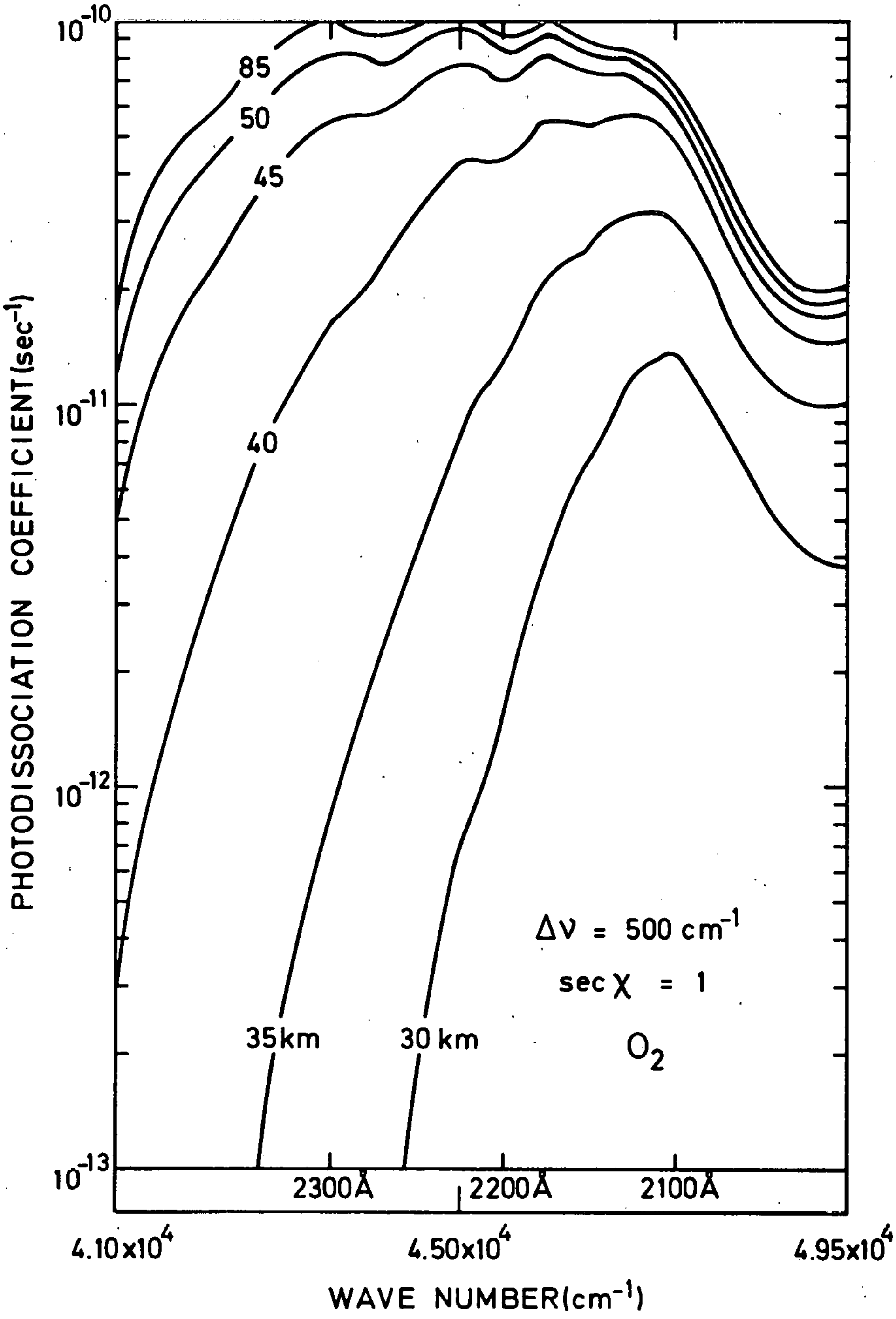

Fig. 3.- Photodissociation coefficients of molecular oxygen in the stratosphere for spectral ranges corresponding to $\Delta \nu$ = 500 cm^{-1} between 2400 A and 2000 A.

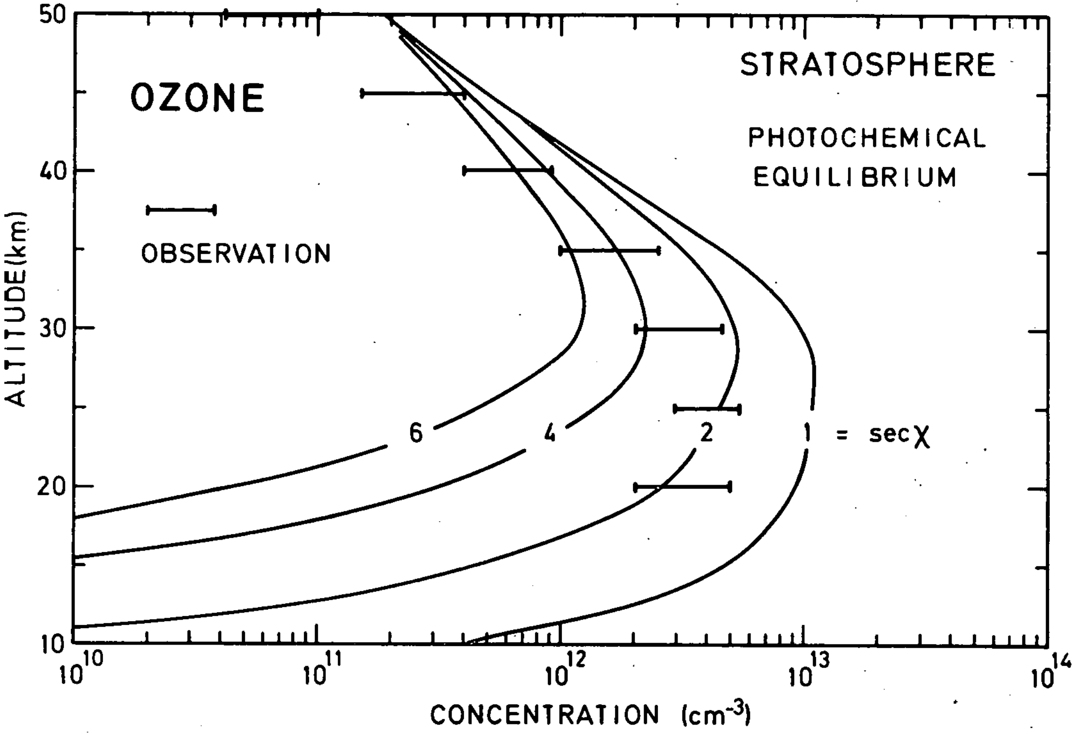

Fig. 4.- Ozone concentrations for photochemical equilibrium conditions compared with observational data. χ is the solar zenith angle.

either a decrease in J_2 or an increase in the effective value of J_3. A decrease in J_2 may be due to a simultaneous reduction in the photodissociation cross sections and in the solar flux over the 2300 - 2000 A spectral range. A careful analysis of the spectral absorption in the Herzberg continuum is required since the absorption cross sections are very small (Ditchburn and Young, 1962 ; Shardanand, 1969 ; Ogawa, 1971 ; Hasson and Nicholls, 1971). A reduced solar flux has been suggested (see Wilson, 1966). A reduction in the effective value of J_3 may be due to an effect of HO_x (Hampson, 1964 ; Roney, 1965) or of NO_x (Crutzen, 1970 ; Johnston, 1971). Instead of (11) an equivalent equation may be written as follows (Nicolet, 1970, 1971).

$$n_*^2(O_3) = \frac{k_2}{k_3} n(M) n^2(O_2) \frac{J_2}{J_3(1 + A)} \qquad (15)$$

where A is a correction term of the form

$$A = \frac{a\ n(HO_x) + b\ n(NO_x)}{k_3\ n(O_3)} \qquad (16)$$

and a and b are the rate coefficients of the reactions of HO_x and NO_x, respectively, with atomic oxygen.

The reduction of the photochemical values $n_*(O_3)$ to the observed values was considered by Crutzen (1970) and Johnston (1971) by including an NO_x effect leading to an increasing mixing ratio of nitrogen oxide with altitude in the stratosphere. Near the stratopause the correction term must also include the effect of the hydrogen compounds. Above the tropopause the catalytic chain involving OH and HO_2 with O_3 (McGrath and Norrish, 1958) which was introduced in order to remove ozone (see, for example, Hung, 1966 ; Hesstvedt, 1968 ; Leovy, 1969, etc) seems unlikely since the rate coefficients which were adopted are too large.

It appears, therefore, that the difficulty has not yet been resolved. In the upper part of the stratosphere (see Fig. 5a) the equilibrium

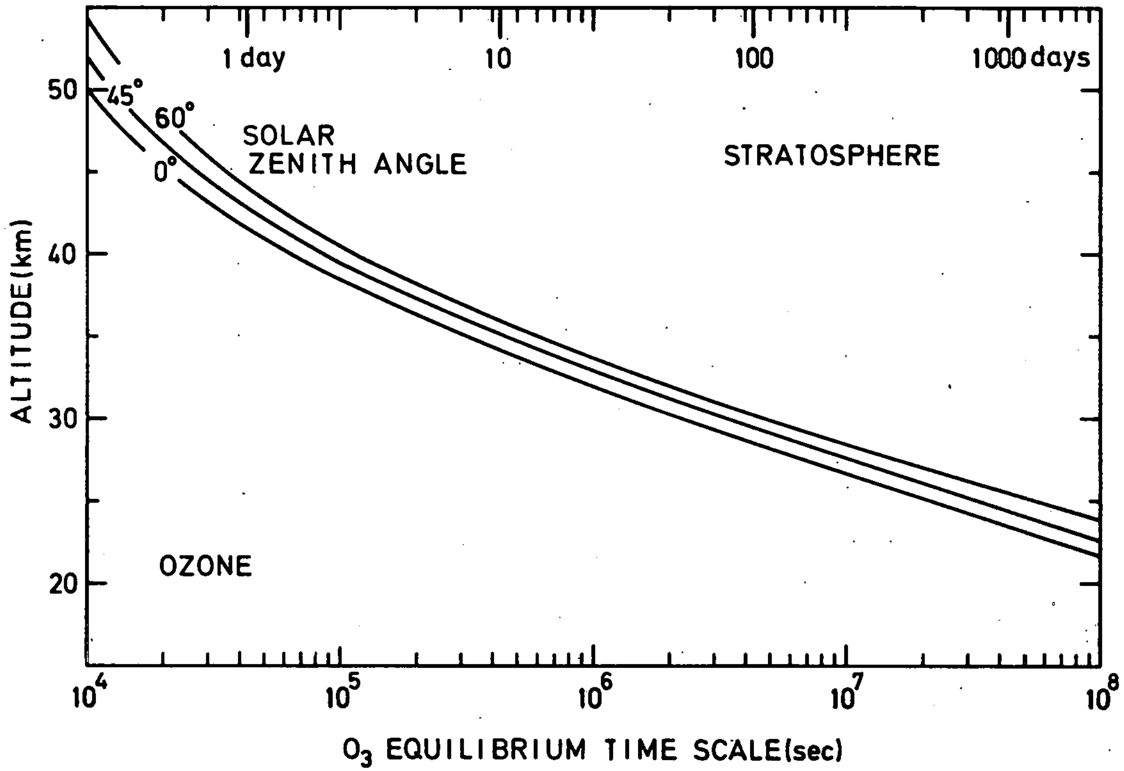

Fig. 5a.- The time to reach equilibrium increases from less than a day at the stratopause to more than a year at 25 km.

times are short and the ozone concentration is insensitive to atmospheric transport. In the lower stratosphere (Fig. 5b) the equilibrium ozone concentration depends strongly on zenith angle and the O_3 concentration is controlled by downward transport. There is a complete departure from photochemical equilibrium conditions since equilibrium times are greater than 1 year and dynamic considerations must be introduced. Thus, instead of (9), the general equation becomes, (16)

$$\frac{\partial n(O_3)}{\partial t} + \text{div}\left[n(O_3)\, w_{O_3}\right] + \frac{2\, k_3\, J_3}{k_2\, n(M)\, n(O_2)} \left\{ n^2(O_3) + a\, n(HO_x) + b\, n(NO_x) \right\}$$

$$= 2\, n(O_2)\, J_2 \tag{17}$$

where w_{O_3} is the transport velocity of O_3.

III. THE HYDROGEN-OXYGEN ATMOSPHERE

The production of $O(^1D)$ atoms by the photolysis of the stratospheric ozone is important. A precise determination depends on the exact efficiency of $O(^1D)$ production in the processes

$$O_3 + h\nu(\lambda < 3100A) \rightarrow O_2\,(^1\Delta_g) + O(^1D) \tag{18a}$$

and

$$O_3 + h\nu(\lambda < 4000\ A) \rightarrow O_2(^3\Sigma_g^-) + O(^1D) \tag{18b}$$

According to DeMore and Raper (1966), all oxygen atoms are $O(^1D)$ at $\lambda \leq 3100$ A ; for $\lambda > 3100$ A there is a drop in the efficiency leading to $O(^3P)$ atoms at 3340 A. (Jones and Wayne, 1969).

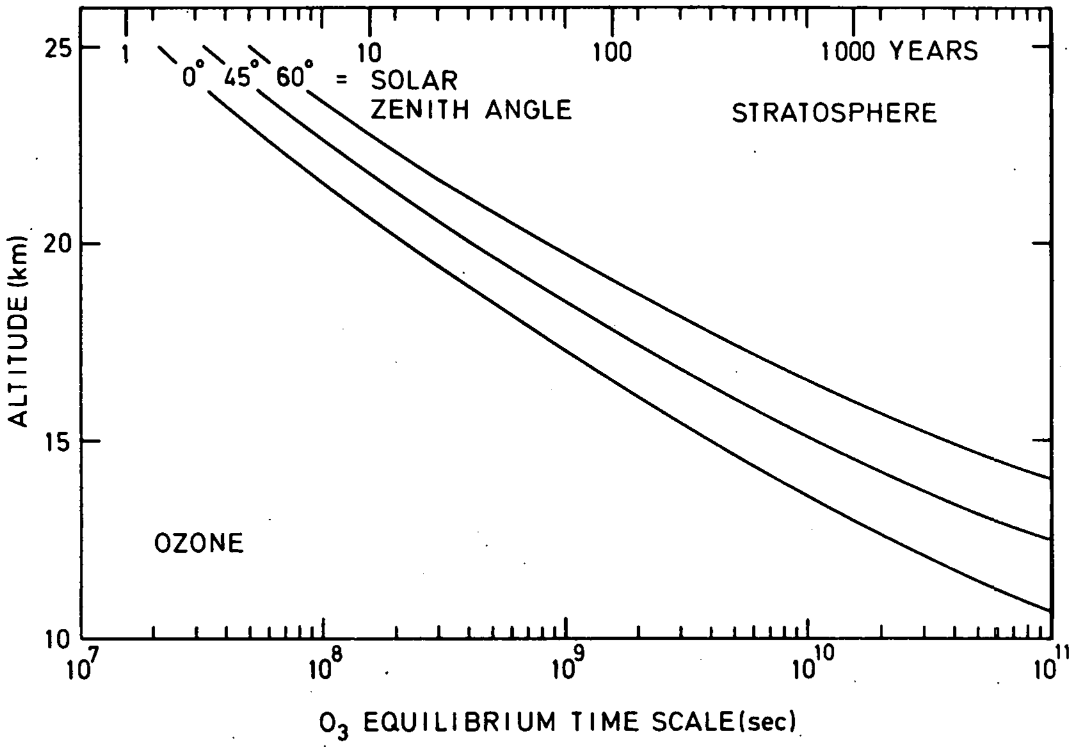

Fig. 5b.- There is a departure from photochemical equilibrium conditions in the lower stratosphere since the O_3 equilibrium times increases from 1 year at 25 km to more than 100 years at 15 km.

Two extreme values of the $O(^1D)$ production have been adopted, and considering the following working value for the quenching rate coefficient

$$k_Q(^1D) = 5 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}^{-1} \tag{19}$$

due to N_2 and O_2 (see, for example, Young et al. 1968 ; Paraskevopoulos and Cvetanovic, 1969 ; DeMore, 1970 ; Noxon, 1970), the photoequilibrium values of $O(^1D)$ concentrations for various solar zenith angles are illustrated in Fig. 6. At the stratopause the variation is small but, in the lower statosphere, the values depend significantly on zenith angle and are sensitive to the spectral efficiency of $O(^1D)$ production which is chosen from the experimental data.

The study of the reaction of $O(^1D)$ with H_2O, CH_4 and H_2 is an important step in the analysis of the aeronomic behavior in the stratosphere. The following reactions occur

$$O(^1D) + H_2O \rightarrow OH + OH^*\ (v \leq 2) + 28.8\ \mathrm{kcal} \tag{20}$$

$$O(^1D) + CH_4 \rightarrow CH_3 + OH^*\ (v \leq 4) + 43.5\ \mathrm{kcal} \tag{21}$$

$$O(^1D) + H_2 \rightarrow H + OH^*\ (v \leq 4) + 43.5\ \mathrm{kcal} \tag{22}$$

Thus the presence of $O(^1D)$ atoms leads to the possibility of the production of H atoms and OH radicals by H_2O, H_2 and CH_4 in the stratosphere. With the fractional volume concentrations that can be adopted (see Nicolet, 1971 for references and explanation) as conventional values at the tropopause for H_2 (0.5×10^{-6}), for CH_4 (1.5×10^{-6}) and for H_2O (3×10^{-6}), the total production $P(HO_x)$ of HO_x radicals at the bottom of the stratosphere is

$$P(HO_x) = 13 \times 10^{-6}\ n(M)\ .\ n^*(O)\ a^* \tag{23}$$

where a^* is the rate coefficient for (20), (21) and (22). Such a coefficient

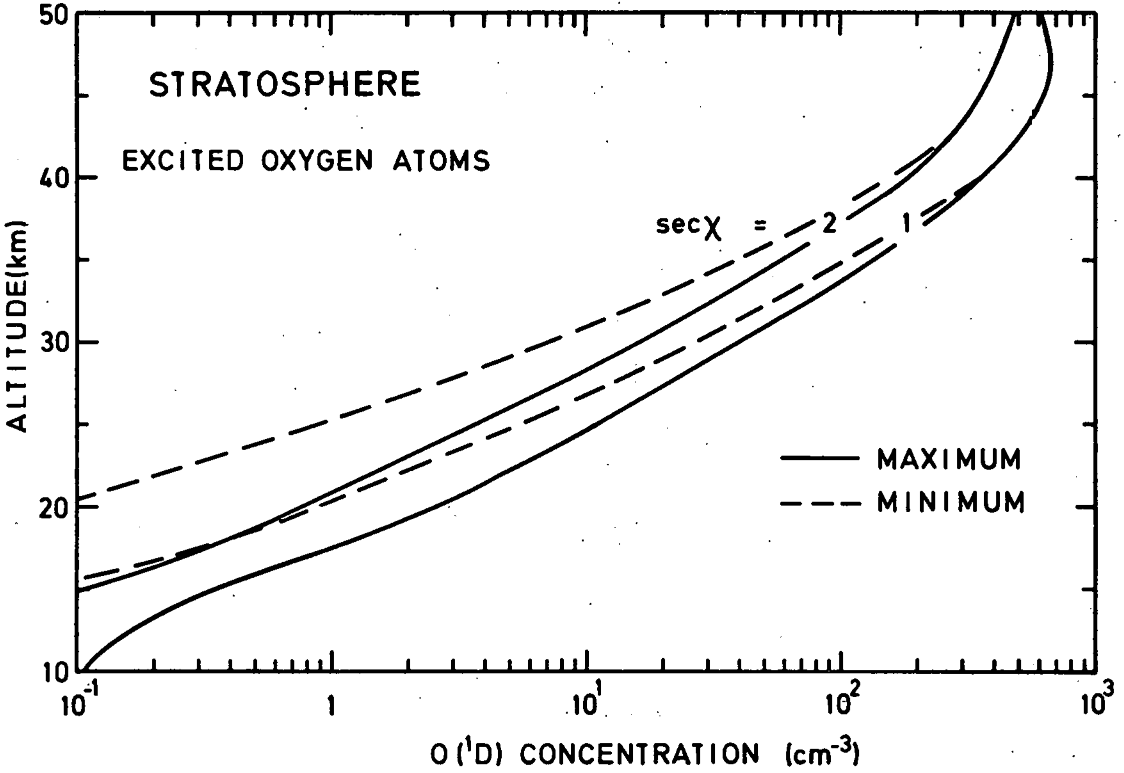

Fig. 6.- Concentration of excited oxygen atoms for two solar zenith angles and two different (minimum and maximum) productions.

has a value greater than 10^{-10} cm^3 sec^{-1} (Nicolet, 1970, 1971). Recent experimental analysis (Young et al. 1968 ; Donovan et al. 1970 ;Paraskevopoulos and Cvetanovic, 1971 ; Heicklen et al. 1971) leads to

$$a^* = (3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \qquad (24)$$

Thus the production of HO_x in the stratosphere near the tropopause may attain

$$P(HO_x) \simeq 10^{-4}\, n(O_3)\, J_3^* \qquad (25)$$

where J_3* is the photodissociation rate coefficient leading to $O(^1D)$ atoms. Numerical results lead to a production of OH radicals from the H_2O dissociation of not less than 10^4 cm^{-3} sec^{-1} above 20 km for an overhead sun and reaching 7 x 10^4 cm^{-3} sec^{-1} in the upper stratosphere.

Inspection of the reactions introduced by Bates and Nicolet (1950) indicates that, in the stratosphere (Nicolet, 1971) a large number of them can be ignored when the rate coefficients are sufficiently well known.

At the stratopause level, a three-body reaction involving atomic hydrogen and molecular oxygen leads to a hydroperoxyl radical

$$(a_1)\ ;\ H + O_2 + M \rightarrow HO_2 + M + 46 \text{ kcal}\ . \qquad (26)$$

The rate coefficient based on measurements made at low temperature by Clyne and Thrush (1963b) and Larkin and Thrush (1964) has a negative temperature coefficient

$$a_1\, n(M) = 3.3 \times 10^{-33}\, e^{800/T}\, n(N_2, O_2) \text{ cm}^3 \text{ sec}^{-1}\ . \qquad (27)$$

At the stratopause, and in the upper part of the stratosphere, the reaction of H with O_3 cannot be neglected ;

$$(a_2) \; ; \; H + O_3 \rightarrow O_2 + OH^*_{v \leq q} + 77 \text{ kcal} \tag{28}$$

has practically no activation energy (Kaufman, 1964) and

$$a_2 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \tag{29}$$

corresponding to the experimental value of $(2.6 \pm 0.5) \times 10^{-11}$ cm^3 sec^{-1} at 300 °K (Philips and Schiff, 1962). The dependence on temperature indicated by a plus one-half power in (29), and other reactions, shows that the activation energy must be small and that a measurement over the 150 - 300 °K temperature range is required. Such a form also shows that there is a certain steric hindrance factor, as it can be seen when (29) is compared with a conventional value, relevant to the present reactions, of $1.5 \times 10^{-11} T^{1/2}$ as given by the elementary kinetic theory of elastic spheres.

Thus, it may be concluded that hydrogen atoms are immediately transformed into hydroperoxyl radicals in the stratosphere since relation (27) is rapid (see Table II). However, at and in the neighbourhood of the stratopause, reaction (28), which leads to OH, cannot be forgotten.

An important reaction which forms a chain leading to the re-formation of oxygen molecules with the production of hydrogen atoms, in conjunction with reaction (28), is the bimolecular process

$$(a_5) \; ; \; OH + O \rightarrow H + O_2 + 16.6 \text{ kcal} \tag{30}$$

Laboratory data (Clyne and Thrush, 1963a ; Kaufman, 1964, 1969 ; Breen and Glass, 1970) lead to values of a_5 from $(5 \pm 2) \times 10^{-11}$ cm^3 sec^{-1} between 265 °K and 293 °K to $(4.3 \pm 1.3) \times 10^{-11}$ cm^3 sec^{-1} at 300 °K. A working value

$$a_5 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \tag{31}$$

is adopted with a possible error of 50 %. With the conventional value of the

TABLE II.- Aeronomic rate coefficients in the stratosphere

Altitude (km)	$a_1\ n(M)\ n(O_2)$ (sec^{-1})	$a_2\ n(O_3)$ (sec^{-1})	$a_5\ n(O)$ (sec^{-1})
15	4.7×10^5	2.4×10^1	2.4×10^{-6}
20	7.7×10^4	6.4×10^1	4.2×10^{-5}
25	1.4×10^4	7.3×10^1	3.0×10^{-4}
30	2.6×10^3	6.7×10^1	1.8×10^{-3}
35	4.6×10^2	4.8×10^1	1.1×10^{-2}
40	1.2×10^2	2.5×10^1	6.0×10^{-2}
45	2.3×10^1	7.9	1.8×10^{-1}
50	6.8	2.5	3.3×10^{-1}

ozone concentration which is adopted here (Table I) the loss coefficient of OH is given in Table II.

It is clear that reaction (30), if it is rapid in the major part of the stratosphere, is relatively slow in the lower stratosphere where other processes may be more important. The chain reaction introduced by McGrath and Norrish (1958)

$$(a_6)\ ;\ OH + O_3 \rightarrow HO_2 + O_2 \qquad (32)$$

and

$$(a_{6b})\ ;\ O + HO_2 \rightarrow OH + O_2 \qquad (33)$$

as the potent ozone-destroying mechanism can be neglected. No direct measurement has been reported. An upper limit $a_6 \geqq 5 \times 10^{-13}$ cm^3 sec^{-1} at room temperature (Kaufman, 1964, 1969) was adopted (Hampson, 1966 ; Hunt, 1966 ; Dütsch, 1968 ; Hesstvedt, 1968 ; Leovy, 1969 ; Shimazaki and Laird, 1970) as the actual value in the stratosphere and mesosphere. A recent analysis by Langley and McGrath (1971) shows that a_6 should be less than 10^{-16} cm^3 sec^{-1} at room temperature. With a steric hindrance factor of the order of 10^{-2} and an activation energy of about 6 kcal, a_6 should be not more than

$$a_6 = 1.5 \times 10^{-13}\ T^{1/2}\ e^{-3000/T} \qquad (34)$$

leading to $a_6\ n(O_3) < a_5\ n(O)$ in the entire stratosphere. Furthermore, reaction (33) which was introduced with a rate coefficient

$$a_{6b} = 5 \times 10^{-14}\ cm^3\ sec^{-1}\ , \qquad (35)$$

must be rejected (DeMore, 1967 ; Nicolet, 1970). Measurements of reactions (32) and (33) are required at 200 °K which corresponds to the temperature of the lower stratosphere.

Instead of reaction (33) the reaction leading to OH involves atomic oxygen (Kaufman, 1964)

$$(a_7)\ ;\ O + HO_2 \rightarrow O_2 + OH^*_{v \leq 6} + 55\ \text{kcal.} \qquad (36)$$

No measurement of reaction (36) has been made. Considering the work of Foner and Hudson (1962), Kaufman (1964) suggests that $a_7 \geq 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}$. Reactions (36) and (30) must be compared since they represent, in the major part of the stratosphere and mesosphere, the chain reaction which is involved in the ozone destroying mechanism through the direct attack of oxygen atoms and re-formation of oxygen molecules.

The values of the rate coefficients a_5 and a_7 which are generally adopted (Hampson, 1966 ; Hunt, 1966 ; Hesstvedt, 1968 ; Dütsch, 1968 ; Crutzen, 1969 ; Leovy, 1969, etc) give

$$a_5/a_7 = 5 \times 10^{-11}/10^{-11} = 5. \qquad (37)$$

Since no direct measurement of reaction (36) has been reported, the ratio $a_5/a_7 = 5$ cannot be invoked to explain the aeronomic behavior of OH and HO_2. The following value is adopted here for a_7, (see remark for a_2),

$$a_7 = 1.5 \times 10^{-12}\ T^{1/2}\ \text{cm}^3\ \text{sec}^{-1} \qquad (38)$$

with the possibility that the ratio a_5/a_7 is not known with sufficient precision and may be between 10 and 1. According to a recent analysis of the HO_2 reactions by Hochanadel *et al.*(1972), their experimental results can be simulated if a value of the order of $7 \times 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}$ is used for a_7. There is, therefore, a possibility that $a_5/a_7 \simeq 1$. In any case, experimental data are needed in order to determine the ratio a_5/a_7 which must be known exactly for the calculation of the ratio $n(HO_2)/n(OH)$ in the stratosphere and mesosphere.

Expressions for the equilibrium ratios of $n(OH)/n(H)$ and $n(HO_2)/n(H)$ can be easily obtained if it is assumed, as a first approximation, that only reactions (26) to (36) are involved. Thus

$$\frac{n(OH)}{n(H)} = \frac{a_1\ n(M)\ n(O_2) + a_2\ n(O_3)}{a_5\ n(O)} \qquad (39)$$

$$\frac{n(HO_2)}{n(H)} = \frac{a_1\ n(M)\ n(O_2)}{a_7\ n(O)} \qquad (40)$$

and

$$\frac{n(OH)}{n(HO_2)} = \frac{a_1\ n(M)\ n(O_2) + a_2\ n(O_3)}{a_1\ n(M)\ n(O_2)} \cdot \frac{a_7}{a_5} \ . \qquad (41a)$$

The ratio given by (41a) must be used at the stratopause (see Table II), but below 40 km it becomes

$$\frac{n(OH)}{n(HO_2)} \simeq \frac{a_7}{a_5} \ . \qquad (41b)$$

In the lower stratosphere, hydroxyl and hydroperoxyl radicals are involved in other important reactions with minor constituents which do not belong to the hydrogen-oxygen atmosphere. CO and NO must be considered since they can react with OH and HO_2, respectively. Among all possible reactions (Nicolet, 1971 ; Levy, 1971 ; McConnel et al. 1971) it seems that these two reactions are the most important processes at and above the tropopause.

A simplified reaction scheme is illustrated in Fig. 7 for the hydroxyl radical. The radical OH is produced by reactions (20), (21) and (22) of $O(^1D)$ atoms with H_2O, CH_4 and H_2 molecules. Reactions of ozone (28) and of atomic oxygen (36) with H atoms and HO_2 radicals, respectively, lead

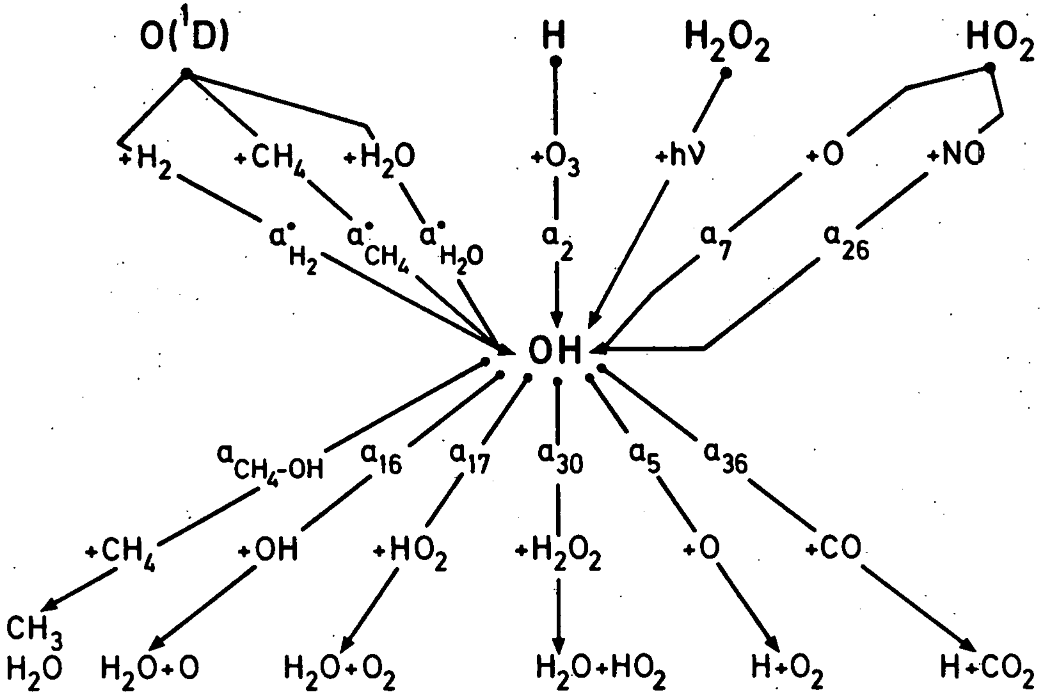

Fig. 7.- Reaction scheme of the hydroxyl radical in a hydrogen-oxygen atmosphere.

also to OH radicals. The photodissociation of hydrogen peroxide cannot be excluded ; the process is

$$(J_{H_2O_2}) \ ; \ H_2O_2 + h\nu \rightarrow 2\ OH \qquad (42)$$

with a photodissociation rate coefficient (Fig. 8) which is not less than 10^{-6} sec^{-1} in the stratosphere. The following reactions (Nicolet, 1965,1970), in which nitrogen oxides are involved,

$$(a_{26}) \ ; \ NO + HO_2 \rightarrow NO_2 + OH + 9\ kcal \qquad (43)$$

$$(a_{32}) \ ; \ NO + H_2O_2 \rightarrow HNO_2 + OH + 11\ kcal \qquad (44)$$

$$(a_{33}) \ ; \ NO_2 + H_2O_2 \rightarrow HNO_3 + OH + 11\ kcal \qquad (45)$$

also lead to OH radicals. However, (44) and (45) are very slow reactions ($< 5 \times 10^{-20}$ cm^3 sec^{-1}) which cannot play a role in the stratosphere according to recent measurements made by Gray, Lissi and Heicklen (1972). The rate coefficient a_{26} is not well known ; nevertheless, it seems that working values of the order of 5×10^{-13} cm^3 sec^{-1} are needed (Levy, 1971) at ground level and it is certain that such a reaction must play a role in the lower stratosphere where $a_7\ n(O)$ is less than 10^{-5} sec^{-1}. A precise experimental determination of the rate coefficient is needed for the analysis of the exact action of nitric oxide on the ratio $n(HO_2)/n(OH)$ in the lower stratosphere.

On the other hand, the radical OH, if it reacts rapidly with atomic oxygen (reaction 30) in the stratosphere, also has a role when H_2O_2, H_2, CO and CH_4 are present. The processes (46), (48), (50) and (52), shown below, have been observed :

$$(a_{30}) \ ; \ OH + H_2O_2 \rightarrow H_2O + HO_2 + 30\ kcal \qquad (46)$$

with rate coefficient (Greiner, 1968)

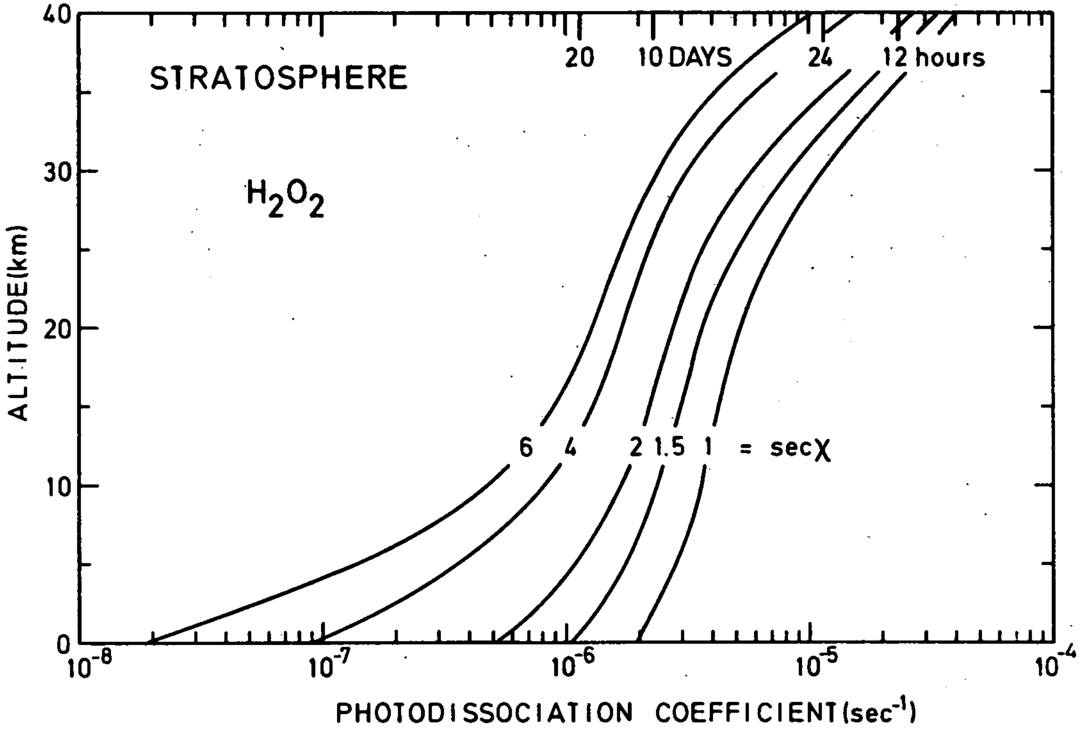

Fig. 8.- Photodissociation coefficient of hydrogen peroxide in the stratosphere for various solar zenith angles χ.

$$a_{26} = 4.1 \times 10^{-13}\ T^{1/2}\ e^{-600/T} \qquad (47)$$

which leads to a rate coefficient of about 3 x 10^{-13} cm^3 sec^{-1} at 200 °K.

$$(a_{19})\ ;\ OH + H_2 \rightarrow H_2O + H + 15\ kcal \qquad (48)$$

with the rate coefficient (Greiner, 1969)

$$a_{26} = 7 \times 10^{-12}\ e^{-2000/T} \qquad (49a)$$

or

$$a_{26} = 2 \times 10^{-13}\ T^{1/2}\ e^{-1800/T} \qquad (49b)$$

which leads to about 5 x 10^{-16} cm^3 sec^{-1} at 200 °K.

$$(a_{36})\ ;\ OH + CO \rightarrow CO_2 + H + 24\ kcal \qquad (50)$$

with the rate coefficient (Greiner, 1969)

$$a_{36} = (1.25 \pm 0.25) \times 10^{-13}\ cm^3\ sec^{-1} \qquad (51)$$

for temperatures of the lower stratosphere.

$$(a_{38})\ ;\ OH + CH_4 \rightarrow H_2O + CH_3 + 15\ kcal \qquad (52)$$

with the rate coefficient (Greiner, 1970)

$$a_{38} = 5 \times 10^{-12}\ e^{-\ 1900/T}\ cm^3\ sec^{-1} \qquad (53a)$$

or

$$a_{38} = 2 \times 10^{-13}\ T^{1/2}\ e^{-\ 1750/T}\ cm^3\ sec^{-1} \qquad (53b)$$

which leads to about 5×10^{-16} cm^3 sec^{-1} at 200 °K. It must be pointed out that reactions (46), (48) and (52) lead to the formation of water vapor. Very precise rate coefficients are required for these reactions involving OH since they play a role in the lower stratosphere where the temperature is not far from 200 °K. In addition, the following loss processes of OH lead to the re-formation of H_2O

$$(a_{16}) \; ; \; OH + OH \rightarrow H_2O + O + 17 \text{ kcal} \tag{54}$$

$$(a_{17}) \; ; \; OH + HO_2 \rightarrow H_2O + O_2 + 72 \text{ kcal} \tag{55}$$

Several measurements of reaction (54) have been made (Kaufman, 1964, 1969 ; Westenberg and deHaas, 1965 ; Dixon-Lewis <u>et al</u>. 1966, Wilson and O'Donovan, 1967 ; Mulcahi and Smith, 1971). Experimental values are well represented by a value of about 2×10^{-12} at 300 °K. With a working value of 1 kcal for the activation energy, a_{16} can be written

$$a_{16} = 7.5 \times 10^{-13} \; T^{1/2} \; e^{-500/T} \tag{56}$$

leading to about 9×10^{-13} cm^3 sec^{-1} at 200 °K. However, at sufficiently high pressures (lower stratosphere, for example) reaction (54) is replaced by

$$(a_{16\,M}) \; ; \; OH + OH + M \rightarrow H_2O_2 + M \tag{57}$$

with a rate coefficient (Caldwell and Back, 1965)

$$a_{16\,M} = 4 \times 10^{-30} \; cm^6 \; sec^{-1} \tag{58}$$

leading to 8×10^{-12} cm^3 sec^{-1} at 20 km .

The reaction (55) is extremely important in the stratosphere and mesosphere since it must be used to determine $n(OH)\, n(HO_2)$ before determining the OH and HO_2 concentrations. In 1964, Kaufman suggested that

$a_{17} \geq 10^{-11}$ cm^3 sec^{-1}. Almost all aeronomic studies treated this as an exact value but such an assumption was not appropriate for the analysis of the ozone problem in the stratosphere. Recent measurement by Hochanadel et al. (1972) indicate that the rate coefficient

$$a_{17} = 2 \cdot x\ 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \tag{59a}$$

i.e. an extremely rapid reaction.

With such a high value of the rate coefficient, it is possible to consider that reaction (55) is the principal process leading to the re-formation of water vapor in the mesosphere. In the upper stratosphere a constant mixing ratio of H_2O corresponding to 3 ppmv leads to $n(OH)\ n(HO_2) > 10^{14}$ cm^{-6}, The values of the hydroxyl and hydroperoxyl concentrations depend on the various reactions which are involved between OH and HO_2. With two arbitrary constant ratios $n(HO_2)/n(OH) = 9$ and 1, the OH concentrations are given in Table IIIa, if only H_2O is involved in the production of OH radicals and if reaction (55) between OH and HO_2 is the re-formation process of H_2O. Such examples are introduced here to show that important errors may occur in the aeronomic analysis and that experimental data are urgently needed in order to determine the exact ratio $n(HO_2)/n(OH)$.

Before ending this discussion concerning the hydroxyl and hydroperoxyl radicals, the two-body process

$$(a_{27})\ ;\ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 + 42 \text{ kcal} . \tag{60}$$

If it is assumed that the rate coefficient a_{27} cannot be too different from a_{16} as it was indicated by indirect laboratory measurements (Foner and Hudson, 1962 ; Dixon-Lewis and Williams, 1962 ; Kaufman, 1964) the following value should be noted

$$a_{27} = 7.5 \times 10^{-13}\ T^{1/2}\ e^{-\ 500/T} \text{ cm}^3 \text{ sec}^{-1} \quad . \tag{61a}$$

TABLE IIIa.- Examples of hydroxyl radical concentrations [n(H_2O) = 3 ppm ; n(HO_2)/n(OH) = 9 or 1 ; solar conditions : between sec χ = 1 and 2]

Altitude (km)	n(HO_2)/n(OH) = 9	n(HO_2)/n(OH) = 1
15	$(1.1 \pm 0.3) \times 10^6$	$(3 \pm 1) \times 10^6$
20	$(2.0 \pm 0.5) \times 10^6$	$(6 \pm 2) \times 10^6$
25	$(2.8 \pm 0.6) \times 10^6$	$(8 \pm 2) \times 10^6$
30	$(3.5 \pm 0.7) \times 10^6$	$(1 \pm 0.2) \times 10^7$
35	$(4.5 \pm 0.9) \times 10^6$	$(1.4 \pm 0.2) \times 10^7$
40	$(5.4 \pm 0.8) \times 10^6$	$(1.6 \pm 0.3) \times 10^7$
45	$(5.2 \pm 0.8) \times 10^6$	$(1.6 \pm 0.2) \times 10^7$
50	$(4.1 \pm 0.3) \times 10^6$	$(1.2 \pm 0.1) \times 10^7$

However, recent measurements by Hochanadel et al.(1972) lead to almost 4 times the value given by (61a) since the laboratory results at 298 °K give

$$a_{27} = (9.5 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \tag{62b}$$

This value is higher than another recent estimate by Paubert (1969).

An idea of the behavior of hydrogen peroxide can be obtained with the simplified equation, based only on (42) and (60),

$$\frac{dn(H_2O)}{dt} + n(H_2O_2)\, J_{H_2O_2} = a_{27}\, n^2(HO_2) \tag{62}$$

The relation $n(HO_2) \leqq n(H_2O_2)$ is valid at the stratopause if $n(HO_2) \geqq 10^7$ cm^{-3}, and in the lower stratosphere (~ 20 km), if $n(HO_2) \geqq 10^6$ cm^{-3}, when photoequilibrium conditions are used for (62).

Finally, considering equilibrium conditions for HO_2 and OH, the following equations are obtained (cf. fig. 9)

$$n(HO_2)\,[a_7\ n(O) + a_{26}\ n(NO) + a_{17}\ n(OH) + 2\ a_{27}\ n(HO_2)] =$$

$$n(OH)\ [a_5\ n(O) + a_{36}\ n(CO) + 2\ a_{38}\ n(CH_4)] \tag{63}$$

and, (Fig. 7),

$$a^*\ n^*(O)\ [n(H_2O) + n(CH_4) + n(H_2)] =$$

$$n(OH)\ [a_{38}\ n(CH_4) + a_{17}\ n(HO_2) + a_{16}\ n(OH)] \tag{64a}$$

In the upper stratosphere (63) and (64) are written as follows

$$\frac{n(OH)}{n(HO_2)} = \frac{a_7}{a_5} \tag{41b}$$

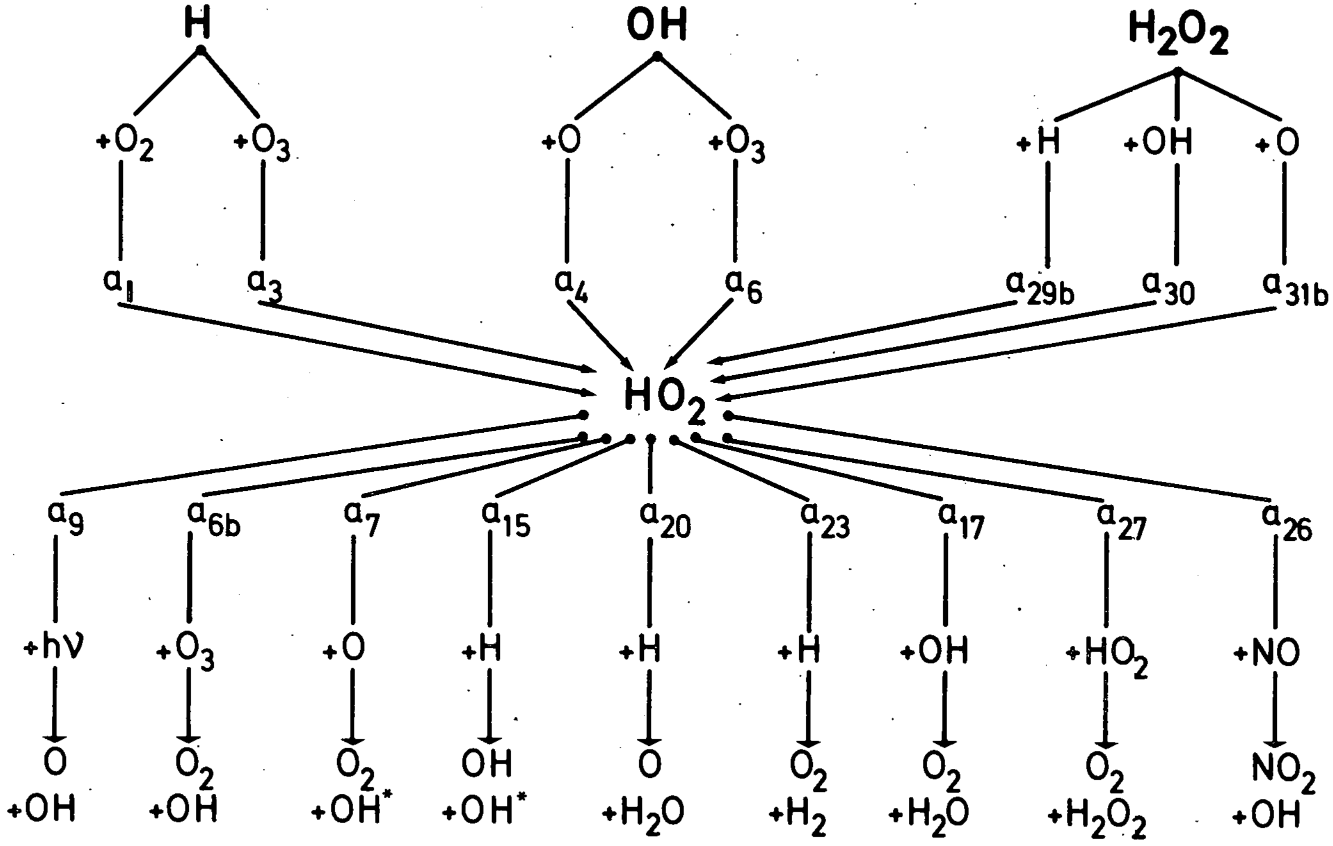

Fig. 9.- Reaction scheme of the hydroperoxyl radical in a hydrogen-oxygen atmosphere.

and

$$[n(CH_4) + n(H_2) + n(H_2O)]\, a^*\, n^*(O) = a_{17}\, n(HO_2)\, n(OH) \;. \qquad (65)$$

Numerical results based on equation (65) are given in Table IIIb. However, in the lower stratosphere for daytime conditions

$$\frac{n(OH)}{n(HO_2)} = \frac{a_7\, n(O) + a_{26}\, n(NO)}{a_5\, n(O) + a_{36}\, n(CO)} \qquad (66a)$$

and at the tropopause for daytime conditions

$$\frac{n(OH)}{n(HO_2)} = \frac{a_{26}\, n(NO)}{a_{36}\, n(CO)} \;. \qquad (66b)$$

As far as (64) is concerned, it may be assumed, in the lower stratosphere and particularly near the tropopause level, that

$$[n(CH_4) + n(H_2) + n(H_2O)]\, a^*\, n^*(O) \geq a_{38}\, n(OH)\, n(CH_4) \qquad (64b)$$

which leads to a determination of the concentration of hydroxyl radicals

$$n(OH) \leq \frac{a^*\, n^*(O)\, [n(CH_4) + n(H_2) + n(H_2O)]}{n(CH_4)\, a_{38}} \;. \qquad (67a)$$

With numerical values (see Table IIIb) corresponding to mixing ratios, 0.5 ppmv for H_2, 1.5 ppmv for CH_4 and 3 ppmv for H_2O, $n(OH) = (4 \pm 2) \times 10^5$ cm^{-3} at 15km for solar conditions varying from an overhead sun to a zenith angle of 60°, $n(OH) = (2 \pm 1) \times 10^6$ at 20 km and $n(OH) = (6 \pm 2) \times 10^6$ cm^{-3} at 25 km. Thus, the OH concentrations in the lower stratosphere decrease when methane is present and values given in Table IIIa below 25 km are too high.

TABLE IIIb.- Examples of hydroxyl radical concentrations

[n(H_2O) = 3 ppm ; n(CH_4) = 1.5 ppm ; n(H_2) = 0.5 ppm ; CH_4 effect]

Altitude (km)	sec χ = 1 (overhead sun)	= 1.4 χ = 45°	= 2 χ = 60°
15	6.7×10^5	3.8×10^5	1.9×10^5
20	3.6×10^6	2.1×10^6	1.2×10^6
25	1.0×10^7	5.9×10^6	3.5×10^6

After sunset, instead of (67a), we must write

$$\frac{1}{n(OH)} \frac{dn(OH)}{dt} = - a_{38} \, n(CH_4) \qquad (67b)$$

which shows that OH is rapidly transformed into H_2O since the life time of OH radicals is relatively short in the lower stratosphere. With a loss coefficient of the order of 3×10^{-3} sec^{-1} at 20 km, the initial concentration of hydroxyl radicals is reduced to 10^{-5} in a very short time of the order of 3 hours. Furthermore, equation (66a) cannot be applied since atomic oxygen is present only in the daytime atmosphere. Finally, NO is transformed into NO_2 in the nighttime stratosphere and equation (66b) cannot be used.

If the mixing ratios of NO and CO above the tropopause were 4×10^{-9} and 4×10^{-8}, respectively, equation (66b) indicates that the ratio $n(HO_2)/n(OH)=10\ a_{36}/a_{26}$ which would be of the order of 1 if $a_{26} \simeq 10^{-12}$ $cm^3 sec^{-1}$.

If the mixing ratios of NO and CO in the lower stratosphere are taken as 4 ppbv and 40 ppbv, respectively, equations (66a) and (66b) indicate that the ratio $n(HO_2)/n(OH)$ depends on the carbon monoxide and nitric oxide concentrations. With $a_{26} \simeq 10\ a_{36}$, $n(HO_2)/n(OH) \simeq 1$. Near 30 km the role of oxygen atoms is important.

Thus, the importance of reactions with hydrogen compounds in the photochemistry of ozone and atomic oxygen in the lower stratosphere depends strongly on the actions of carbon monoxide and of nitric oxide. The action of methane must be introduced in the process of H_2O re-formation above the tropopause level.

Finally, instead of (9), the rate of change of O_3 in the stratosphere must be written (Nicolet, 1966, 1970)

$$\frac{dn(O_3)}{dt} + \frac{J_3}{k_2\ n(M)\ n(O_2)}\ n(O_3)[2\ k\ n(O_3) + a_5\ n(OH) + a_7\ n(HO_2)]$$

$$= 2n(O_2)\ J_2 \qquad (68a)$$

In the upper stratosphere (68a) becomes, using (41b),

$$n(O_3) = \frac{k_2}{k_3}\ n(M)\ n(O_2)\ \frac{n(O_2)\ J_2}{n(O_3)\ J_3 + a_5\ n(OH)} \qquad (68b)$$

IV. NITROGEN OXYGEN ATMOSPHERE

In a pure oxygen atmosphere the photochemical destruction of ozone is given by reaction (8)

$$O_3 + O \rightarrow O_2 + O_2 \qquad (69)$$

and in a hydrogen-oxygen atmosphere by a catalytic cycle of an HO-HO_2 system involving reactions (30) and (36) in the stratosphere

$$O + OH \rightarrow H + O_2 \qquad (70)$$

$$O + HO_2 \rightarrow OH + O_2 \qquad (71)$$

In a nitrogen-oxygen atmosphere the catalytic cycle involves NO and NO_2 (Crutzen,1970 ; Johnston, 1971 ; Nicolet, 1971). Nitric oxide reacts with ozone as follows

$$(b_4)\ ;\ NO + O_3 \rightarrow NO_2 + O_2 + 48\ \text{kcal} \qquad (72)$$

with a rate coefficient which is sufficiently well known (Johnston and Crossby, 1954 ; Clyne, Thrush and Wayne, 1964)

$$b_4 = 1 \times 10^{-12} \, e^{-1250/T} \, . \tag{73}$$

NO_2 is subject to photodissociation

$$(J_{NO_2}) \; ; \; NO_2 + h\nu(\lambda < 3975 \text{ A}) \rightarrow NO + O \, . \tag{74}$$

The photodissociation rate coefficient is about 4×10^{-3} $\sec^{-1}$ at 50 km and it is not less than 3×10^{-3} $\sec^{-1}$ at 15 km. An average value of $(3.4 \pm 0.5) \times 10^{-3}$ $\sec^{-1}$ may be adopted in the stratosphere.

However, the following reaction plays a role in the upper stratosphere

$$(b_3) \; ; \; O + NO_2 \rightarrow NO + O_2 + 46 \text{ kcal} \tag{75}$$

It is relatively a rapid reaction (Schiff, 1964 ; Klein and Herron, 1964 ; Westenberg and deHaas, 1969). At 200 °K, the extrapolation of such experimental data leads to 2 and to 7×10^{-12} cm^3 $\sec^{-1}$ which may be given either by

$$b_{3a} = 5 \times 10^{-13} \, T^{1/2} \, cm^3 \sec^{-1} \tag{76a}$$

or by

$$b_{3b} = 1 \times 10^{-12} \, T^{1/2} \, e^{-350/T} \, cm^3 \sec^{-1} \, . \tag{76b}$$

An unpublished result (Davis, 1972) gives

$$b_{3c} = 9.2 \times 10^{-12} \, cm^3 \sec^{-1} \tag{76c}$$

over the 235 - 350 °K temperature range.

Thus, this is again a clear illustration that the experimental values of many rate coefficients must be known with greater accuracy for the study of aeronomic processes in the stratosphere.

Considering that (72), (74) and (75) are the principal reactions in the stratosphere, (Nicolet, 1965),

$$\frac{dn(NO_2)}{dt} + n(NO_2)[J_{NO_2} + b_3\, n(O)] = b_4\, n(NO)\, n(O_3) \tag{77a}$$

and, for daytime conditions since $1/J_{NO_2} \leqslant 3 \times 10^2$ sec,

$$\frac{n(NO_2)}{n(NO)} = \frac{b_4\, n(O_3)}{J_{NO_2} + b_3\, n(O)} \tag{77b}$$

With the numerical values adopted here (73) and (76c), the $n(NO_2)/n(NO)$ ratio is given in Table IV at various altitudes and for two values of the zenith angle. The ratio increases from about 1 at 15 km to nearly 4 at 30 km and decreases above 35 km to the order of 2×10^{-2} at 50 km. Thus, the daytime ratio $n(NO_2)/n(NO)$ should be of the order of 1 in the lower stratosphere, but is related to the ozone variation.

Thus, if we introduce the effect of nitrogen oxides (NO and NO_2) in the ozone equation (9), we must write from (72), (74) and (75),

$$\frac{dn(O_3)}{dt} + \frac{J_3\, n(O_3)}{k_2\, n(M)\, n(O_2)} [2k_3\, n(O_3) + b_4\, n(NO) + b_3\, n(NO_2)]$$

$$= 2n(O_2)\, J_2 + n(NO_2)\, J_{NO_2} \tag{78}$$

which becomes, with (77),

$$\frac{dn(O_3)}{dt} + \frac{2\, J_3\, n(O_3)}{k_2\, n(M)\, n(O_2)} [k_3\, n(O_3) + b_3\, n(NO_2)] = 2n(O_2)\, J_2 \tag{78b}$$

TABLE IV.- Ratio $n(NO_2)/n(NO)$ in the stratosphere

Altitude (km)	Solar zenith angle	
	sec χ = 1	sex χ = 2
15	$0.9^{(1)}$	$0.95^{(1)}$
20	2.7	2.9
25	3.6	3.8
30	$3.6^{(2)}$	$3.7^{(2)}$
35	2.7	2.7
40	0.6	0.9
45	8.9×10^{-2}	1.4×10^{-1}
50	1.6×10^{-2}	2.1×10^{-2}

(1) only effect of J_{NO2} alone

(2) also effect of b_3 n(O)

Comparing (78) with (68), which involves the effect of hydroxyl and hydroperoxyl radicals, the ozone concentration in the upper stratosphere is given by

$$n(O_3) = \frac{k_2}{k_3}\, n(M)\, n(O_2)\; \frac{n(O_2)\, J_2}{n(O_3)\, J_3 + a_5\, n(OH) + b_3\, n(NO_2)} \tag{78c}$$

which shows that the correction term to J_3 [see (15) and (16)] can be written

$$A = \frac{a_5\, n(OH) + b_3\, n(NO_2)}{k_3\, n(O_3)} \tag{79}$$

Table V shows that the same effect is obtained for a ratio $n(OH)/n(NO_2)$ of the order of 10^{-1}. For example, if between 35 km and 40 km the ozone concentration is of the order of 10^{12} cm^{-3}, then from 5×10^7 to about 10^8 OH molecules have the same effect as from 5×10^8 to about 10^9 NO_2 molecules.

In the ozonosphere, various reactions with nitrogen oxides may be considered (see Nicolet, 1965, 1971 ; Johnston, 1971). Among the possible reactions, a three-body association leading to nitrous and nitric acids,

$$(b_{22}) \; ; \; OH + NO_2 + M \rightarrow HNO_3 + M + 53 \text{ kcal}, \tag{80}$$

is an important process for which the rate coefficient, b_{22}, for T = 300 °K is (Simonaitis and Heicklen, 1971)

$$b_{22} = 1.3 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \tag{81a}$$

for M = He, or

$$b_{22} = 1.1 \times 10^{-29} \text{ cm}^3 \text{ sec}^{-1} \tag{81b}$$

if $M = H_2O$.

TABLE V.- Numerical values of $\frac{a_5}{k_3} \frac{n(OH)}{n(O_3)} + \frac{b_{3b}}{k_3} \frac{n(NO_2)}{n(O_3)}$

Altitude (km)	a_5/k_3	b_{3b}/k_3
15	9.6×10^4	6.1×10^3
20	6.8	4.6
25	4.9	3.5
30	3.6	2.7
35	2.0	1.7
40	1.2	1.1
45	1.0	1.0
50	1.0	1.0

With $b_{22} = 5 \times 10^{-30}$ cm^6 sec^{-1} for O_2 and N_2, it can be seen that the life-time of OH is very short in the lower stratosphere if there is no re-formation process of OH. In fact,

$$(b_{27})\ OH + HNO_3 \rightarrow H_2O + NO_3 + 15 \text{ kcal} \tag{82}$$

with a coefficient which, according to Hussain and Norrish(1963), should be of the order of

$$b_{26} = 1.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \tag{83}$$

The possibility of finding a re-formation process for OH from HNO_3 is a photodissociation (see Leighton, 1961)

$$(J_{HNO_3})\ ;\ HNO_3 + h\nu \rightarrow OH + NO_2 \tag{84}$$

Another reaction

$$(b_{28})\ ;\ O + HNO_3 \rightarrow OH + NO_3 \tag{85}$$

is slow, and according to Morris and Niki (1971), its rate coefficient is less than 2×10^{-14} cm^3 sec^{-1}. It seems, therefore, that the relevant differential equation for the HNO_3 concentration is

$$\frac{dn(HNO_3)}{dt} + n(HNO_3)[J_{HNO_3} + b_{27}\ n(OH) + b_{28}\ n(O)]$$

$$= b_{22}\ n(OH)\ n(NO_2)\ n(M) \tag{86}$$

Nighttime equilibrium conditions would lead to

$$\frac{n(HNO_3)}{n(NO_2)} < \frac{b_{22}\ n(M)}{b_{27}} \simeq 10^2 \tag{87a}$$

at 15-20 km. However, according to computations based on equation (67b), the hydroxyl radicals disappear in the lower thermosphere after sunset and, consequently, a nighttime equilibrium cannot be attained for the ratio $n(HNO_3)/n(NO_2)$. Thus, the photodissociation process (84) cannot be eliminated as an effective loss process of HNO_3 in the lower stratosphere since J_{HNO_3} could be greater than 10^{-7} sec^{-1}. Photoequilibrium conditions, which, perhaps, do not exist in the lower stratosphere, lead to

$$\frac{n(HNO_3)}{n(NO_2)} = \frac{n(OH)\ b_{22}\ n(M)}{J_{NO_3} + b_{27}\ n(OH)} \qquad (87b)$$

Once again, exact values of the parameters are needed for a determination of the theoretical ratio $n(HNO_3)/n(NO_2)$. Observational results indicate that the HNO_3 mixing ratio in the lower stratosphere is not less than 10^{-9} (Murcray et al. 1969 ; Rhine et al. 1969) and that the NO_2 mixing ratio is less than 3×10^{-8} (Ackerman and Frimout, 1969).

Thus, it seems that the OH radicals are not only subject to reactions with hydrogen compounds (Fig. 7) but also depend on nitrogen compounds. The equilibrium value in the lower stratosphere would be, to a first approximation (Fig. 10),

$$n(OH) = \frac{a^*\ n^*(O)[n(CH_4) + n(H_2O) + n(H_2)] + n(HNO_3)\ J_{HNO_3}}{a_{38}\ n(CH_4) + b_{22}\ n(M)\ n(O_2) + a_{17}\ n(HO_2)} \qquad (88a)$$

Reducing (88a) to an oversimplified form

$$n(OH) = \frac{a^*\ n^*(O)[n(CH_4) + n(H_2O) + n(H_2)]}{b_{22}\ n(M)\ n(NO_2)} \qquad (88b)$$

can be accepted over the 15-25 km stratospheric region if there is no efficient photodissociation process of nitric acid. From equation (88b), one determines that, with $n(NO_2) = 4 \times 10^{-9}\ n(M)$, the OH concentration would be only between 10^4 cm^{-3} and 10^5 cm^{-3} in the lower part (15-20 km) of the

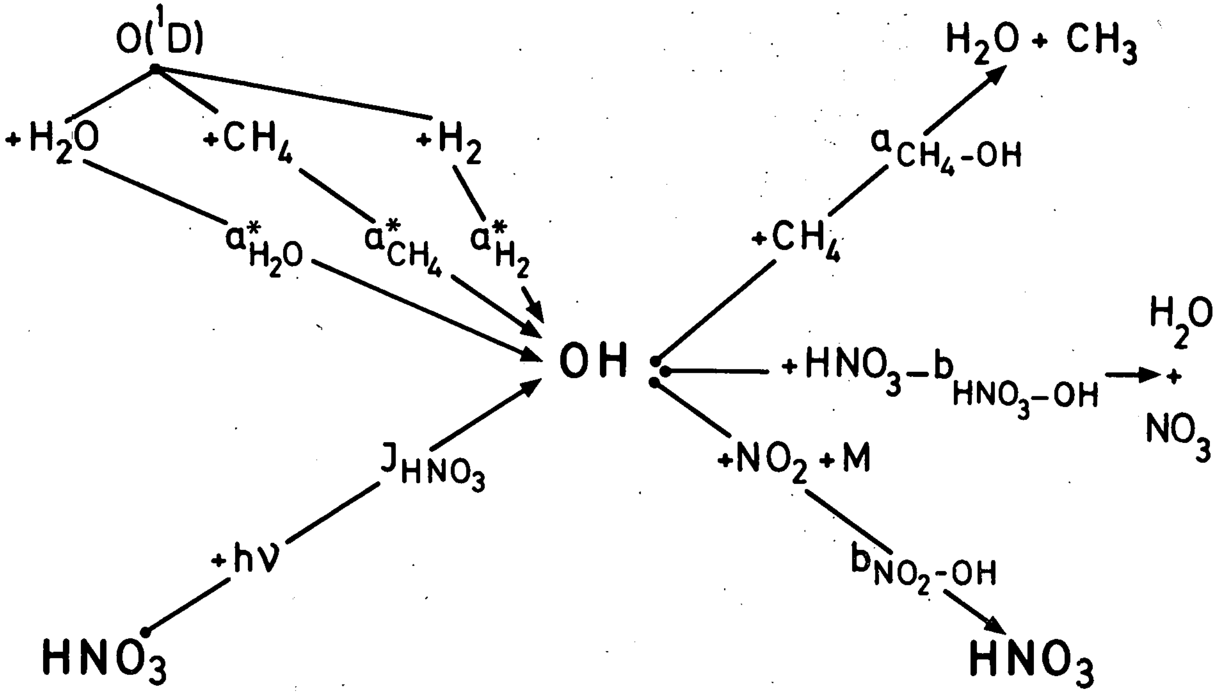

Fig. 10.- Scheme of the principal reactions of hydroxyl radicals above the tropopause in the lower stratosphere.

stratosphere. Table IIIc shows the various concentrations of the OH molecules which are obtained according to the loss process which is involved ; a factor of about 100 can be involved at 15 km and is reduced to less than 10 at 20 km.

Consequently, if there is no active photodissociation process of nitric acid between 15 and 20 km, the OH concentrations are relatively low. Results given in Table IIIc indicate that there are differences with the results of McConnell <u>et al</u>. (1971) ; their computed OH profil indicates an almost constant value of its concentration between the ground level and 20 km. Such different values show that a careful analysis of all aeronomic processes in the lower stratosphere is required before attempting to reach a final conclusion.

The presence of nitrogen oxides in the stratosphere may be related to the downward transport of NO molecules from the mesosphere. In the mesosphere the nitric oxide concentration depends on the photodissociation rate J_{NO} which is related to a predissociation process. For zero optical depth $J_{NO} = 5 \times 10^{-6}$ sec^{-1} and its value decreases rapidly in the mesosphere since the absorption depends on the structure of the (10-0) and (9-0) Schumann-Runge bands of molecular oxygen and of the (1-0) δ bands of nitric oxide (Fig. 11). The differential equation pertaining to the variation of the nitric oxide concentration in the mesosphere

$$\frac{\partial n(NO)}{\partial t} + n(NO)\, J_{NO} + \frac{\partial}{\partial z}\left[n(NO)\; w_{NO}\right] = 0 \qquad (89)$$

becomes

$$\frac{\partial n(NO)}{\partial t} + \frac{\partial}{\partial z}\left[n(NO)\; w_{NO}\right] = 0 \qquad (90)$$

at the stratopause since J_{NO} is very small at that level. Observational values of the NO concentration (Pontano and Hale, 1970) of the order of 10^9 cm^{-3}

TABLE IIIc.- Examples of hydroxyl radical concentrations (cm^{-3}) in the lower stratosphere.

Altitude (km)	Table IIIa (HO_2)	Table IIIb (CH_4)	Effect of HNO_3
15	(1 ± 0.3) to $(3\pm1) \times 10^6$	$(4 \pm 2) \times 10^5$	$(4 \pm 2) \times 10^4$
20	(2 ± 0.5) to $(6\pm2) \times 10^6$	$(2 \pm 1) \times 10^6$	$(1 \pm 0.5) \times 10^5$
25	(3 ± 0.6) to $(8\pm2) \times 10^6$	$(6 \pm 2) \times 10^6$	$(1 \pm 0.6) \times 10^6$

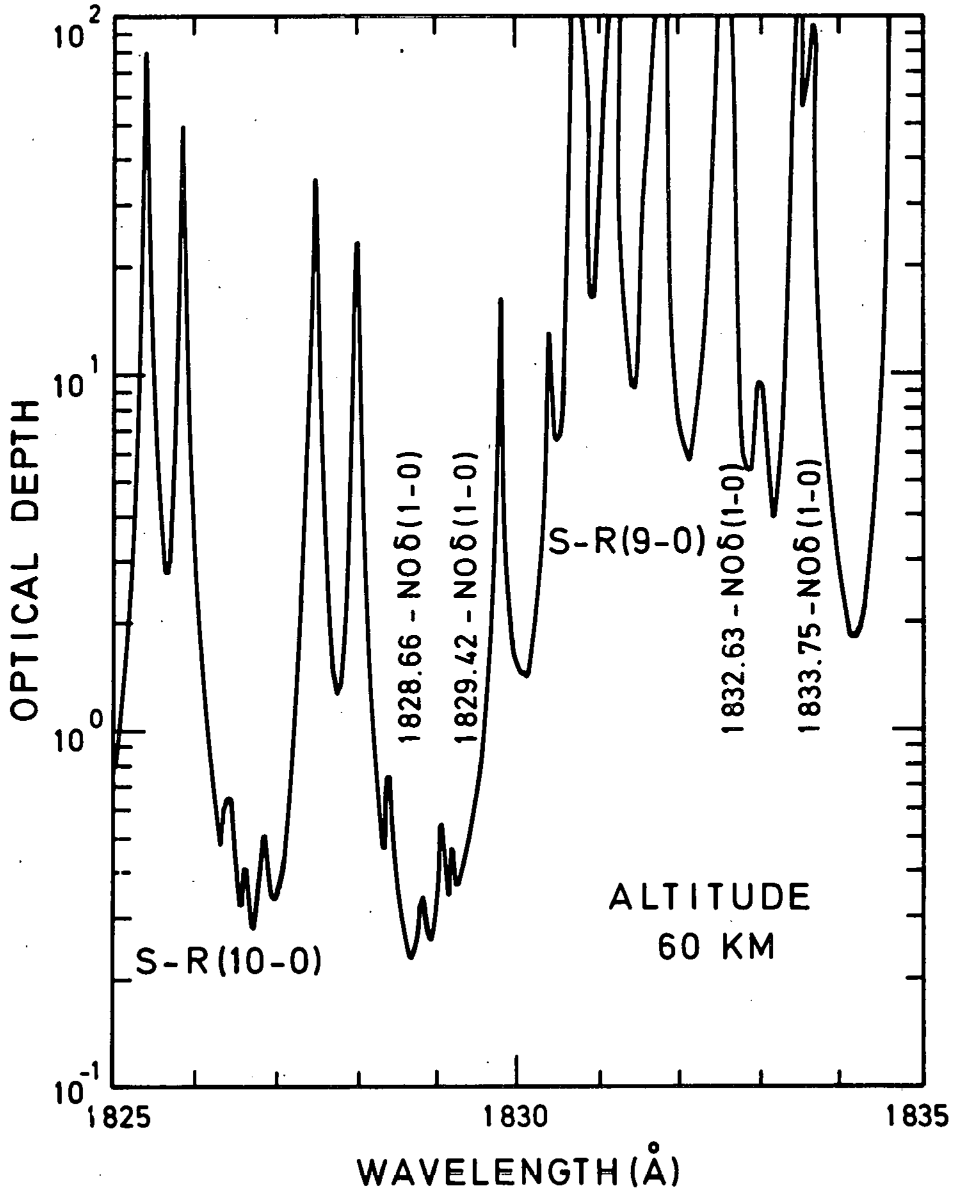

Fig. 11.- The δ bands of nitric oxide are absorbed in the mesosphere by the Schumann-Runge bands of molecular oxygen and determine the photodissociation coefficient.

at the stratopause are larger than the theoretical values deduced by Strobel (1972) $[10^6 < n(NO) < 10^7 \text{ cm}^{-3}]$ and also more than a mixing distribution $[n(NO) \sim 10^8 \text{ cm}^{3}]$ if $[n(NO_2) + n(NO)]/n(M) = 3 \times 10^{-9}$ at the tropopause (Nicolet, 1965).

Nitric oxide is produced in the stratosphere by a reaction between nitrous oxide and the excited oxygen atom in the $O(^1D)$ state (Nicolet, 1970)

$$(b_{38}) \; ; \; O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (91a)$$

$$(b_{39}) \; ; \; O(^1D) + N_2O \rightarrow 2\ NO \qquad (91b)$$

with a global rate coefficient of the order of 2×10^{-10} cm^3 sec^{-1} (Young et al. 1968) and a ratio $b_{38}/b_{39} \simeq 1$ according to Greenberg and Heicklen(1970). Thus the production of NO molecules is given by

$$\frac{dn(NO)}{dt} = 2 \times 10^{-10}\ n(N_2O)\ n[O(^1D)] \text{ cm}^{-3} \text{ sec}^{-1} \qquad (92)$$

Since N_2O is photodissociated by $\lambda < 3400$ A (Bates and Hayes, 1967) leading only to (Nicolet, 1970 ; Nicolet and Vergison, 1971)

$$N_2O + h\nu\ (\lambda \leq 3400 \text{ A}) \rightarrow N_2(X^1\Sigma) + O(^1D) \qquad (93)$$

in the stratosphere, the vertical distribution of nitrous oxide, which does not produce NO by photodissociation, decreases rapidly with height according to the differential equation

$$\frac{\partial n(N_2O)}{\partial t} + \text{div}\,[n(N_2O)\ w_{N_2O}] + n(N_2O)J_{N_2O} = 0 \qquad (94)$$

Examples of the vertical distribution of nitrous oxide with a mixing ratio of 2.5×10^{-7} at the tropopause are illustrated in Fig. 12. It is clear that the distribution depends on the eddy diffusion coefficients which are adopted

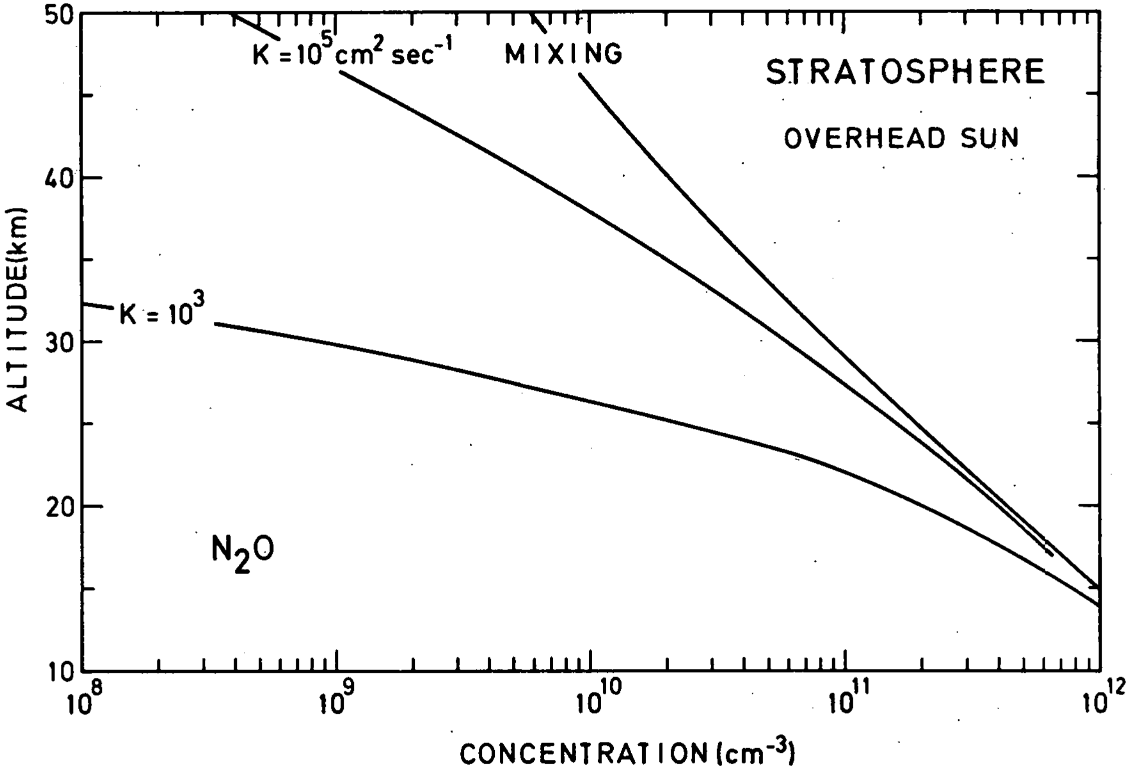

Fig. 12.- Vertical distributions of the nitrous oxide concentration in the stratosphere related to various eddy diffusion coefficients $K = 10^3$ cm^2 sec^{-1}, $K = 10^5$ cm^2 sec^{-1} and mixing.

(Nicolet and Vergison, 1971 ; McElroy and McDonnell, 1971). The measurements in the stratosphere by Schütz *et al.*(1970) and Goldman *et al.*(1970) indicate that more observations are needed in order to determine the stratospheric distribution of N_2O with latitude and altitude.

Nevertheless, it is possible to consider (Nicolet and Vergison, 1970) that the stratospheric production of nitric oxide P_n is of the order of

$$P_n(NO) = (1.5 \pm 1) \times 10^8 \text{ cm}^2 \text{ sec}^{-1} \qquad (95)$$

which is of the same order of magnitude as the artificial injection by 500 supersonic transport aircraft.

Finally, the differential equation pertaining to the variation of nitric oxide in the stratosphere is

$$\frac{\partial n(NO)}{\partial t} + \text{div}\left[n(NO)\, w_{NO}\right] + \text{div}\left[n(HNO_3)\, w_{HNO_3}\right] = P(NO) \qquad (96)$$

where P(NO) is given by (92). The downward transport of nitric acid from the stratosphere into the troposphere may be considered as a destruction process of stratospheric nitrogen oxides. Thus, special attention should be given to atmospheric conditions relating to the tropopause and its multiple structure. The exchange between troposphere and stratosphere must be studied at various latitudes.

V. THE CO AND CH_4 PROBLEM IN THE STRATOSPHERE

Methane, which has been found as a permanent constituent of the troposphere, has continuous sources at ground level. It is dissociated by ultraviolet radiation in the mesosphere and by oxidation processes in the stratosphere (Nicolet, 1971)

The dissociative reactions in the stratosphere are

$$(a^{*}_{CH_4})\ ;\ O(^1D) + CH_4 \rightarrow CH_3 + OH + 43.5\ \text{kcal} \qquad (21)$$

and

$$(a_{38})\ ;\ OH + CH_4 \rightarrow CH_3 + H_2O + 15\ \text{kcal}\ . \qquad (52)$$

In the lower stratosphere CO_2 is photodissociated at a very low rate. In the upper stratosphere the production is not less than 10^3 CO molecules cm^{-3} sec^{-1}. In the lower stratosphere the photodissociation process is less important than the oxidation process (21) which can be considered as follows

$$O(^1D) + CH_4 \rightarrow CO + 4\ H \qquad (97)$$

as far as the CO production is concerned. Methyl radicals which are produced by reactions (21) and (52) react with molecular oxygen

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M + 26\ \text{kcal} \qquad (98)$$

with a rate coefficient of the order of 10^{-31} cm^6 sec^{-1} at room temperature (Heicklen, 1968 ; Spicer et al. 1972) .

Methylperoxy radicals react with oxides of nitrogen via

$$(b_{31a})\ ;\ CH_3O_2 + NO \rightarrow CH_3O_2NO \qquad (99a)$$

or

$$(b_{31b})\ ;\ CH_3O_2 + NO \rightarrow H_2CO + HNO_2 \qquad (99b)$$

as regards NO. The production of methyl peroxynitrite is about 1.5 times the simultaneous production of formaldehyde and nitrous acid. In the same way the reactions with NO_2 are

$$(b_{32a})\ CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2 \qquad (100a)$$

or

$$(b_{32b})\ CH_3O_2 + NO_2 \rightarrow H_2CO + HNO_3 \ . \qquad (100b)$$

Here the production of formaldehyde and nitric acid is about 3 times the production of methylperoxynitrate. There is no evidence for the reaction between CH_3O_2 and NO producing $CH_3O + NO_2$ (Spicer *et al*. 1972).

Finally the photochemistry of formaldehyde (McGuigg and Calbert, 1969) indicates that two distinct primary photodissociation processes occur

$$H_2CO + h\nu \rightarrow H + HCO \qquad (101a)$$

and

$$H_2CO + h\nu \rightarrow H_2 + CO \qquad (102a)$$

which lead to CO and HCO. It should be noted that the photodissociation of formaldehyde leads to the production of molecular hydrogen in the stratosphere.

The photodissociation coefficients of H_2CO based on recently published cross sections (Calvert *et al*. 1972) can be determined. For the production of hydrogen atoms and formyl radicals, the photodissociation coefficient J_{H-HCO} is

$$J_{H-HCO} = 9.4 \times 10^{-5}\ sec^{-1} \qquad (101b)$$

at zero optical depth ; the simultaneous production of molecular hydrogen and carbon moxonide leads to the photodissociation coefficient J_{H_2-CO}

$$J_{H_2-CO} = 1.3 \times 10^{-4} \text{ sec}^{-1} . \qquad (102b)$$

The photodissociation coefficients are given in Table VI at three altitudes in the lower stratosphere and for solar zenith angles between 0° and 60°. Thus, the total photodissociation coefficient of H_2CO is $(1.3 \pm 0.2) \times 10^{-4} \text{sec}^{-1}$ in the lower stratosphere.

A rapid reaction such as

$$H_2CO + OH \rightarrow HCO + H_2O + 36 \text{ kcal} . \qquad (103a)$$

with a rate coefficient (Morris and Niki, 1971)

$$a_{OH-CH_2O} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \qquad (103b)$$

seems to be a less important process in the lower stratosphere than the direct photodissociation process ; it requires OH concentrations greater than 10^7 cm^{-3} to compete with the photodissociation having a coefficient J_{H_2CO} which is of the order of 1.3×10^{-4} sec^{-1} in the lower stratosphere.

Thus, with equations (98) to (101), it is possible to consider that the oxidation of methane leads to the production of carbon monoxide (97) and to the simultaneous production of formaldehyde and nitric acid. The production of formaldehyde $P(CH_2O)$ is given by

$$P(CH_2O) = \frac{0.4\, b_{31}\, n(NO) + 0.75\, b_{32}\, n(NO_2)}{b_{31}\, n(NO) + b_{32}\, n(NO_2)} \left[a^*_{CH_4}\, n^*(O) + a_{38}\, n(OH)\right] n(CH_4) \qquad (103a)$$

$$\simeq \frac{1}{2} \left[a^*_{CH_4}\, n^*(O) + a_{38}\, n(OH)\right] n(CH_4) . \qquad (103b)$$

TABLE VI.- Photodissociation coefficients of formaldehyde (sec^{-1})

Altitude (km)	H - HCO and H_2 - CO	H - HCO	H_2 - CO
15	$(1.2\pm0.1) \times 10^{-4}$	$(3.3\pm0.6) \times 10^{-5}$	$(8.5\pm0.7) \times 10^{-5}$
20	$(1.3\pm0.1) \times 10^{-4}$	$(3.8\pm0.5) \times 10^{-5}$	$(9.5\pm0.6) \times 10^{-5}$
25	$(1.4\pm0.1) \times 10^{-4}$	$(4.3\pm0.5) \times 10^{-5}$	$(1.0\pm0.5) \times 10^{-4}$

From (101), (102) and (103), we may write

$$n(CH_2O) \simeq \frac{[a^* \; n^*(O) + a_{38} \; n(OH)] \; n(CH_4)}{2[J_{H-HCO} + J_{H_2-CO} + 1.5 \times 10^{-11} \; n(OH)]} \qquad (104a)$$

and in the lower stratosphere an oversimplified equation

$$n(CH_2O) \leq \frac{a^* \; n^*(O) \; n(CH_4)}{2 \; J_{H_2CO}} \qquad (104b)$$

since a_{38} n(OH) may be of the same order of magnitude as a^* $n^*(O)$.

With a mixing ratio of CH_4 of the order of 1.5 ppmv between 15 and 25 km, the CH_2O concentrations could reach the following photochemical equilibrium values : $(2 \pm 1) \times 10^6$ cm^{-3} at 15 km, $(9 \pm 5) \times 10^6$ cm^{-3} at 20 km and $(1 \pm 0.5) \times 10^7$ at 25 km. Such concentrations should lead to productions of H_2 molecules of the order of 10^3 cm^{-3} sec^{-1} near 20 km. Reaction (101a) would lead also to the production of hydrogen atoms of about 10^3 cm^{-3} sec^{-1} near 20 km which corresponds to an indirect production of HO_2 radicals. In the same way the formyl radical also leads directly by reaction with O_2 or indirectly by photodissociation to hydroperoxyl radicals in the stratosphere. An additional source of nitric acid which, not previously considered, is given by

$$P(HNO_3) = \frac{0.75 \; b_{32} \; n(NO_2)}{b_{31} \; n(NO) + b_{32} \; n(NO_2)} \; [a^*_{CH_4} \; n^*(O) + a_{38} \; n(OH)] \; n(CH_4) \qquad (105)$$

Such a source increases when the NO_2 and O_3 concentrations increase . The reaction scheme of Fig. 11 shows the relative importance of process (105).

In order to determine the importance of reaction (97) in leading to the production of CO it is necessary to know the vertical distribution of CH_4 in the entire stratosphere. Measurements made in the stratosphere by Bainbridge and Heidt (1966) indicate that the transport of methane $F_K(CH_4)$ across the tropopause is given by

$$F_K(CH_4) = n(CH_4)\ K \left[\frac{1}{H_{CH_4}} + \frac{1}{H_M} \right] \qquad (106)$$

where K is the eddy diffusion coefficient, H_{CH_4} and H_M are the scale height of CH_4 and of the atmosphere respectively and corresponds to an eddy diffusion flux of about 5×10^9 molecules CH_4 cm^{-2} sec^{-1}. Such a transport is equivalent to a stratospheric production of 5×10^9 carbon monoxide molecules cm^{-2} sec^{-1} and also results in an addition of 10^{10} water vapor molecules cm^{-2} sec^{-1} in the stratosphere. Such an addition does not differ greatly from an artificial injection by 500 SST aircraft.

However, an vertical flow of about 5×10^9 CH_4 molecules cm^{-2} sec^{-1} corresponds to an average eddy diffusion coefficient of 2×10^3 cm^2 sec^{-1} which would lead to a decrease of about a factor of 1000 in the mixing ratio of methane from the tropopause to the stratopause. The examples (Fig. 13) of the vertical distribution of methane in the stratosphere show the important differences for two typical values of the average eddy diffusion coefficient $K = 10^3$ and 10^4 cm^2 sec^{-1}. The first observational result (Scholz et al. 1970) leading to $\leq 5 \times 10^{-8}$ for the CH_4 mixing ratio at the tropopause corresponds to $K < 10^4$ cm^2 sec^{-1} but a second analysis (Ehhalt et al. 1972) leading to a CH_4 mixing ratio of 2.5×10^{-7} requires an eddy diffusion coefficient of about 2×10^4 cm^2 sec^{-1}.

If we accept this last result, we must assume that the scale height h of the CH_4 mixing ratio is not less than 20 km. In other words, (see equation 106), if

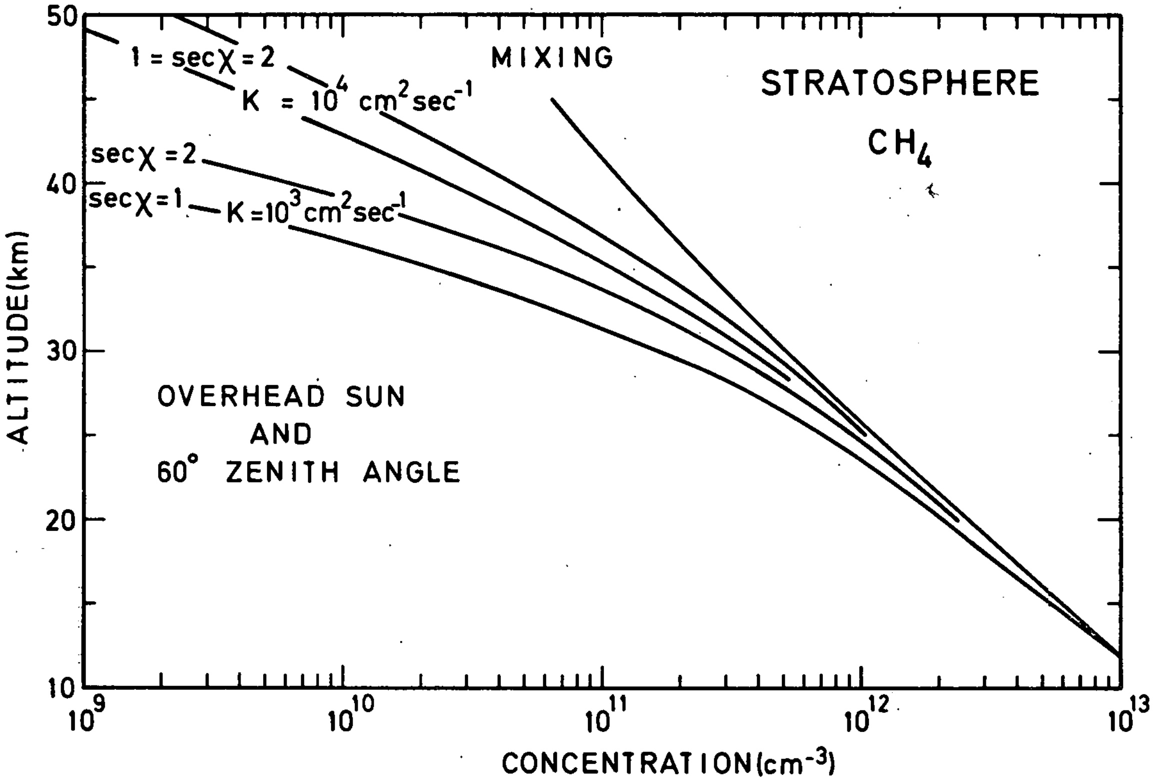

Fig. 13.- Vertical distribution of the methane concentration in the stratosphere for 2 solar zenith distances (0° and 60°) and 2 eddy diffusion coefficients $K = 10^3$ cm^2 sec^{-1} and 10^4 cm^2 sec^{-1} compared with mixing.

$$\frac{1}{h} = \frac{1}{H_{CH_4}} - \frac{1}{H_M} = \frac{1}{2.2 \times 10^6} \tag{107}$$

as given by Bainbridge and Heidt (1966) for their second profile between 15 to 24 km, is extended up to 50 km, the CH_4 mixing ratio decreases from 15 km to 50 km to 20 % of its tropopause value as given by Ehhalt et al. 1972. But, such a relatively high mixing ratio at the stratopause requires an average eddy diffusion coefficient for the total stratosphere greater than 10^4 $cm^2 sec^{-1}$. Such a high value indicates that new observational results are needed.

As far as carbon monoxide is concerned the general equation for its vertical distribution in the stratosphere must be written as follows :

$$\frac{\partial n(CO)}{\partial t} + \mathrm{div}\,[n(CO)\, w_{CO}] + a_{36}\, n(OH)\, n(CO) =$$

$$n(CO_2)\, J_{CO_2} + n(CH_4)\, [a^* \, n^*(O) + a_{38}\, n(OH)] \tag{108a}$$

At the stratopause, there is a photochemical equilibrium (Hays and Olivero, 1970) ; the principal process for the production of carbon monoxide is the photodissociation of carbon dioxide and the principal loss process is the reaction of CO with OH radicals since the transport is too slow. Instead of (108a), the photochemical conditions may be considered as follows

$$n(CO_2)\, J_{CO_2} = a_{36}\, n(OH)\, n(CO) \tag{108b}$$

In the major part of the stratosphere the CO production is due to the oxidation process of methane by excited oxygen atoms $O(^1D)$ and by the reaction of OH with methane. However, in the lower stratosphere the dissociative reaction of CH_4 with $O(^1D)$ is a very slow process and below 25 km the reaction between OH and CH_4 is the principal process even for small concentrations of the hydroxyl radical.

In the lower stratosphere there is a decrease of carbon monoxide (Seiler and Junge, 1969). Its corresponds to a very rapid decrease of the mixing ratio above the tropopause (Seiler and Warneck, 1972) from the tropospheric ratio $(1.4 \pm 0.2) \times 10^{-7}$ to another mixing ratio of the order of 4×10^{-8}. Such results (Junge <u>et al</u>. 1970) ; Seiler and Warneck, 1972) show that the mixing ratio decreases to 1/e of its tropopause in about 1 km. Thus

$$\frac{n(CO)}{n(M)} = \frac{n_{tr}(CO)}{n_{tr}(M)} . e^{-z/h} \equiv \frac{n_{tr}(CO)\ e^{-z/H_1}}{n_{tr}(CO) . e^{-z/H}} \tag{109}$$

with

$$\frac{1}{h} = \frac{1}{H_1} - \frac{1}{H} = \frac{1}{10^5} \tag{110}$$

In this transition region the transport leads to

$$F_{CO} = n_{tr}(CO)\ w(CO) = n(CO)\ K \left(\frac{1}{H_1} - \frac{1}{H} \right) \tag{111a}$$

and with (110)

$$F_{CO} = n_{tr}(CO)\ K/10^5 \text{ cm}^{-2} \text{ sec}^{-1} \tag{111b}$$

With $n_{tr}(CO) = 1.5 \times 10^{12}$ cm^{-3} at the tropopause (≤ 9 km), the vertical flux of CO molecules above the tropopause is

$$F_{CO} = 1.5 \times 10^7 \text{ K cm}^{-2} \text{ sec}^{-1} \tag{111c}$$

which is very important

$$F_{CO} \geq 5 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1} \tag{111d}$$

if the eddy diffusion coefficient is not less than 3×10^3 cm^2 sec^{-1}.

If the CO molecules which are injected by (111d) are removed by the oxidation of CO by OH (Pressman and Warneck, 1970 ; Hesstvedt, 1970), an equivalent recycling of hydroxyl radicals corresponding to more than 10^5 OH radical cm^{-3} sec^{-1} is required.

Furthermore, if the diffusive upward current of CO molecules by eddy diffusion given by (111a) corresponds to the oxidation of CO by OH, we may write

$$n(CO)\ K \left(\frac{1}{H_1} - \frac{1}{H} \right) = n(CO)\ a_{36}\ n(OH)\ H_1 \qquad (112)$$

Equation (112) with $K = 3 \times 10^3$ and $H_1 \simeq 1$ km, leads to $n(OH) > 10^6$ cm^{-3} (Seiler and Warneck, 1972). Such a value is very high when the reaction between OH and CH_4 is considered. With a concentration of about 10^{-2} $O(^1D)$ atoms at 10 km as given by McConnell et al.(1971) it is difficult to produce more than 5×10^2 OH molecules cm^{-3} sec^{-1} and to reach a concentration of 10^6 OH molecules cm^{-3} at 10 km. The loss process by the reaction between OH and CH_4 reaches about 1.5×10^{-2} sec^{-1}.

In conclusion, the aeronomic conditions (Fig. 14) are different in the lower and upper stratosphere. The ratio of the hydroxyl and hydroperoxyl radical concentrations depends on reactions with oxygen atoms in the upper stratosphere but is related to the carbon monoxide and nitric oxide concentrations in the lower stratosphere. Furthermore, the dissociation and re-formation of water vapor are related to the presence of CH_4 and H_2 and their vertical distribution in the lower stratosphere. On the other hand, the nitrogen oxides concentrations depend not only for the vertical transport from or to the stratosphere of NO and NO_2 but also on the formation of nitric acid, on its dissociation process and finally on its downward transport to the troposphere.

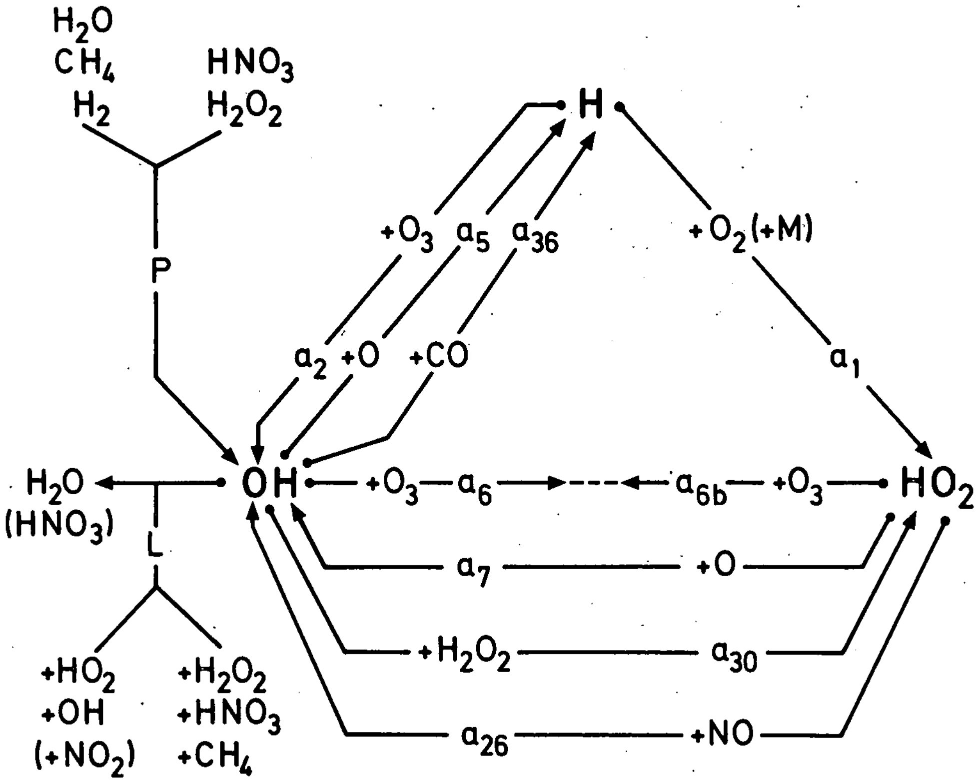

Fig. 14.- Reaction scheme showing the water vapor cycle in the stratosphere.

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