Stratospheric Ozone: An Introduction to Its Study

MARCEL NICOLET

Aeronomy Institute, Brussels, Belgium
Ionosphere Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania   16802

An analysis is made of the various reactions in which ozone and atomic oxygen are involved in the stratosphere. At the present time, hydrogen, nitrogen, and chlorine compounds in the ranges parts per million, parts per billion, and parts per trillion may have significant chemical effects. In the upper stratosphere, above the ozone peak, where there is no strong departure from photochemical equilibrium conditions, the action of hydroxyl and hydroperoxyl radicals of nitrogen dioxide and chlorine monoxide on atomic oxygen and of atomic chlorine on ozone can be introduced. A precise determination of their exact effects requires knowledge of (1) the vertical distribution of the H_2O, CH_4, and H_2 dissociation by reaction of these molecules with electronically excited oxygen atom $O(^1D)$; (2) the ratio of the OH and HO_2 concentrations and their absolute values, which depend on insufficiently known rate coefficients; (3) the various origins of nitric oxide production, with their vertical distributions related to latitude and season; and (4) the various sources giving different chlorine compounds that may be dissociated in the stratosphere. In the lower stratosphere, below the ozone peak, there is no important photochemical production of O_3, but there exist various possibilities of transport. The predictability of the action of chemical reactions depends strongly on important interactions between OH and HO_2 radicals with CO and NO, respectively, which affect the ratio $n(OH)/n(HO_2)$ at the tropopause level; between OH and NO_2, which lead to the formation of nitric acid with its downward transport toward the troposphere; between NO and HO_2, which lead to NO_2 and its subsequent photodissociation; between ClO and NO, which also lead to NO_2 and become more important than the reaction of ClO with O; and between Cl and various molecules, such as CH_4 and H_2, which lead to HCl with its downward transport toward the troposphere. All these chemical processes are subject to many changes since they occur in the lower stratosphere where seasonal, latitudinal, and even day-to-day variations of the ozone concentrations are observed in association with advective and dynamic transports, which depend on meteorological conditions as indicated by variations of tropopause heights.

CONTENTS

HISTORICAL INTRODUCTION

The aeronomy and meteorology of atmospheric ozone have been studied by many scientists since the suggestion made by *Schönbein* [1840a, b] of the existence of an atmospheric constituent having a particular odor (from Greek *ozein*, to smell), its exact origin deduced by *da la Rive* [1845] from an electrical discharge through pure oxygen. Ozone was chemically proved to exist in the troposphere, at ground level, by *Houzeau* [1858]. Its first clear spectroscopic detection related to the atmosphere was made by *Chappuis* [1880, 1882] in the visible part of the spectrum (Chappuis bands). However, during the same period, *Hartley* [1881a] detected in the laboratory the strong ultraviolet absorption spectrum of ozone (Hartley band) below 300 nm. At the same time, he identified [*Hartley*, 1881b] the atmospheric limit of the solar spectrum detected by *Cornu* [1879]. The principal conclusion reached by *Hartley* [1881b] was that ozone is a normal constituent of the higher atmosphere, being in larger proportion there than near the earth's surface, and its quantity is quite sufficient to account for the ultraviolet limitation of the solar spectrum at ground level. As far as the Huggins bands ($\lambda > 300$ nm) are concerned,

they were detected by *Huggins and Huggins* [1890] as a new group of lines in the photographic spectrum of Sirius and finally identified by *Fowler and Strutt* [1917] as absorption bands of atmospheric ozone.

The first quantitative analysis of atmospheric ozone was made by *Fabry and Buisson* [1913, 1921a, b] by a study of the ultraviolet absorption in the Hartley and Huggins bands, leading to the determination of absolute values of the total atmospheric content. But the ozone problem in its general aspects was really developed after the first world war, as can be seen from the publication by *Fabry* [1929] of 27 papers presented at a meeting in Paris at which, as a result of his observational work, Dobson had introduced the real meteorological significance of atmospheric ozone [*Dobson and Harrison*, 1926, 1927; *Dobson et al.*, 1929; *Dobson*, 1930]. At the same meeting, *Chalonge and Götz* [1929] had shown that their daytime and nighttime observations by a spectroscopic method did not detect any variation in the total content of atmospheric ozone. The first theoretical approach was also given at this Paris conference (May 1929) on atmospheric ozone by *Chapman* [1930], who had introduced the first aeronomic analysis of the ozone problem. However, in 1930, it was not yet possible to reach a general understanding, since the ozone peak was misplaced at an average height of about 45 km. A detailed analysis of the main known facts regarding atmospheric ozone at that time is given by *Fabry and Buisson* [1930] and *Götz* [1931].

The first measurements of the vertical distribution of stratospheric ozone were obtained by an indirect method introduced by Götz in 1929 [*Dobson*, 1968] during his various observations at Spitzbergen. It is called the Umkehr method and was further developed by *Götz et al.* [1934]. The principal results showed that the average height of the ozone layer is only of the order of 25 km and that the main changes in ozone

content appear to be centered between 10 and 20 km, a fact of real meteorological significance. The literature on the subject can be found in a summary published by *Götz* [1938], and complete accounts of the important advances in the experimental and theoretical aspects of atmospheric ozone are given [*Craig*, 1950] for the period before direct soundings made with optical instruments were introduced [*Kulcke and Paetzold*, 1957; *Vassy*, 1958] and for the present using chemical sondes [*Regener*, 1960; *Brewer and Milford*, 1960]. Since 1965, the use of chemical instruments has been the basis for the first analysis of meridional cross sections of the vertical ozone distribution [*Griggs*, 1966; *Dütsch*, 1969, 1971].

Today the rocket observations [*Krueger*, 1973], and particularly the continous survey of the stratospheric ozone field by satellites [*Prabhakara et al.*, 1973; *Heath et al.*, 1973; *Krueger et al.*, 1973], are leading to the possibility of an analysis on a planetary scale. However, when a detailed study of the ozone exchange between the stratosphere and troposphere is required, particularly in the region of the jet stream where the most significant exchanges of air take place, it is still necessary to derive information from a synoptic analysis, as was done by *Piaget* [1969, 1971]. A great amount of effort is still needed to understand the atmospheric movements in the neighborhood of the tropopause.

Stratospheric ozone is therefore of real meteorological and aeronomic significance as a result of the work which was accomplished during the last 50 years.

The photochemical theory put forward by *Chapman* [1930, 1943] was first developed for a pure oxygen atmosphere [*Mecke*, 1931; *Wulf and Deming*, 1936a, b, 1937; *Dütsch*, 1946; *Craig*, 1950] and therefore was greatly idealized. However, 25 years ago, vibrational rotational bands of the hydroxyl radical OH, which were identified in the airglow, [*Meinel*, 1950], aroused interest in the photochemistry of hydrogen-oxygen compounds [*Bates and Nicolet*, 1950a; *Herzberg*, 1951] and in particular of methane [*Bates and Nicolet*, 1950b] and of water vapor [*Bates and Nicolet*, 1950c]. The photochemistry of atmospheric water vapor, leading to the action of hydroxyl and hydroperoxyl radicals on the ozone distribution, was studied in considerable detail by *Bates and Nicolet* [1950c]. In 1950, the analysis was difficult because of the grievous lack of reliable basic data, and the study was limited only to the mesosphere and lower thermosphere, where the photodissociation of water vapor and methane occur. But the study of the possible action of hydrogen compounds in the stratosphere became possible when the reaction of H_2O with the electronically excited atomic oxygen in the ^1D state was indicated as a dissociation process by *Cadle* [1964] and *Hampson* [1964]. The concentrations of $O(^1D)$ produced by ozone photolysis in the stratosphere (and troposphere) are sufficiently large to lead to OH radicals, not only from water vapor but also from methane and molecular hydrogen [*Nicolet*, 1970a]. However, the application to the stratosphere, with numerical rate coefficients for reactions of O_3 with OH and HO_2 [*Hampson*, 1966; *Hunt*, 1966; *Dütsch*, 1968; *Hesstvedt*, 1968; *Leovy*, 1969; *Crutzen*, 1969], has been difficult to accept because of the uncertainty of the arbitrarily assumed values of the principal parameters, particularly in the lower stratosphere. Only very recent laboratory measurements indicate that the hydrogen compounds cannot explain the ozone behavior below the stratopause (≤ 40 km), and it has been proposed by *Crutzen* [1970] and emphasized by *Johnston* [1971] that oxides of nitrogen can play a leading role in the stratospheric ozone distribution. Subsequent work [*Johnston*,

1972, 1974; *Johnston and Whitten*, 1973; *Nicolet*, 1971, 1972, 1974; *Crutzen*, 1971, 1973, 1974a; *Dütsch*, 1973; *McElroy et al.*, 1974; *Wofsy and McElroy*, 1974] has led to the conclusion that NO_2 is a dominant odd oxygen destroyer, at least above the ozone peak.

Finally, stratospheric chlorine (see article by *Ryan and Mukherjee* [1975] in this volume for a description of sources of stratospheric gaseous chlorine) has been introduced by *Stolarski and Cicerone* [1974] as a possible sink for ozone. After some hesitation [*Crutzen*, 1974a; *Wofsy and McElroy*, 1974] its role has been recognized [*Clyne and Watson*, 1974; *Cicerone et al.*, 1974, 1975b; *Crutzen*, 1974b; *Wofsy et al.*, 1975a] since its possible action has been demonstrated in various papers by *Molina and Rowland* [1974a, b] and *Rowland and Molina* [1975] in which the effect of industrial cholrofluoromethanes and of tropospheric carbon tetrachloride was introduced. Ultimately, the action of natural methyl chloride [*Lovelock*, 1975] with relative concentrations of the order of 10^{-9} should lead, at the present time, to the most important stratospheric chlorine source.

In fact, since all halogens (bromine, fluorine, chlorine, and iodine) act as catalysts in the ozone destruction processes, their aeronomic properties should be considered with their natural and industrial sources when all experimental rate coefficients, which are needed, are determined with accuracy. Attention has been focused recently on atmospheric bromine by *Wofsy et al.* [1975b].

OZONE FORMATION AND DESTRUCTION

In order to describe the stratospheric problems of ozone formation and destruction, it is necessary to consider the various reactions in a certain order. The first step is to introduce the reactions in a pure oxygen atmosphere, as given by *Chapman* [1930, 1943], without horizontal or vertical transfer of ozone. The second step is the introduction of hydrogen compounds into the photochemical treatment of the ozone problem, as was done by *Bates and Nicolet* [1950c], with the effect of the electronically excited atomic oxygen in the ^1D state as introduced in the stratosphere by *Hampson* [1964]. The action of nitrogen oxides on ozone introduced by *Crutzen* [1970] will be studied by considering the various reactions that are involved in the stratosphere [*Nicolet*, 1965a, 1971; *Crutzen*, 1971; *Johnston*, 1971]. The problem of methane oxidation requires special attention in the lower stratosphere; the various reactions must be considered in detail [*Levy*, 1971, 1972, 1973; *McConnell et al.*, 1971; *Wofsy et al.*, 1972; *Nicolet and Peetermans*, 1973]. Finally, the role of chlorine compounds must be discussed [*Clyne and Watson*, 1974; *Watson*, 1974; *Molina and Rowland*, 1975] in order to determine the role of the ClO_x cycle in depleting stratospheric ozone. It should be noted that the details on all reactions have been distributed over several years by the Chemical Kinetics Information Center, National Bureau of Standards [e.g., *Garvin and Hampson*, 1974; *Hampson and Garvin*, 1975] and will be published in a monograph of the Climatic Impact Assessment Program (Department of Transportation, Washington, D. C.).

REACTIONS IN A PURE OXYGEN STRATOSPHERE

When dissociation of molecular oxygen occurs the oxygen atoms liberated by photodissociation may recombine in the presence of a third body (N_2, O_2):

$$(k_1) \qquad O + O + M \rightarrow O_2 + M + 118 \text{ kcal} \qquad (1a)$$
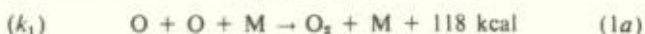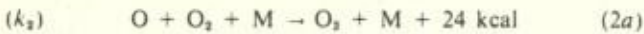
A recent laboratory analysis [*Campbell and Gray*, 1973] at 196

and 298 K leads to a rate coefficient

$$k_1 = 4.7 \times 10^{-33} (300/T)^2 \text{ cm}^3 \text{ s}^{-1} \quad (1b)$$

However, this reaction, which plays a role in the mesosphere, can be neglected in the stratosphere, since oxygen atoms unite with oxygen molecules to form ozone by

(k_2) $\quad\quad O + O_2 + M \rightarrow O_3 + M + 24 \text{ kcal} \quad (2a)$

for which the rate coefficient, which has been measured with good precision by *Huie et al.* [1972] between 200 and 346 K, is

$$k_2 = 1.1 \times 10^{-34} e^{510/T} n(O_2, N_2) \text{ cm}^3 \text{ s}^{-1} \quad (2b)$$

Ozone molecules are destroyed by a two-body collision process

(k_3) $\quad\quad O + O_3 \rightarrow 2O_2 + 94 \text{ kcal} \quad (3a)$
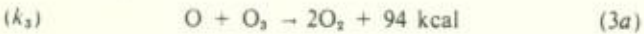
Recent measurements over the temperature range 200–300 K by *Krezenski et al.* [1971], over the temperature range 269–409 K by *McCrumb and Kaufman* [1972], and between 220 and 1000 K [*Davis et al.*, 1973*d*] lead to a value which is not too different from

$$k_3 = 1.1 \times 10^{-11} e^{-2150/T} \text{ cm}^3 \text{ s}^{-1} \quad (3b)$$

Therefore by using (2b) and (3b), the ratio k_2/k_3, which plays an important role in the equilibrium equation of stratospheric ozone, can be written as

$$k_2/k_3 = 10^{-23} e^{2660/T} \text{ cm}^3 \quad (4)$$

If J_2 and J_3 are the photodissociation coefficients of O_2 and O_3, respectively, the equations governing the rates of change of the concentration of ozone and atomic oxygen, $n(O_3)$ and $n(O)$, are

$$[dn(O)/dt] + 2k_1 n(M) n^2(O) + k_2 n(M) n(O_2) n(O)$$
$$+ k_3 n(O_3) n(O) = 2n(O_2) J_2 + n(O_3) J_3 \quad (5)$$

and

$$[dn(O_3)/dt] + n(O_3) J_3 + k_3 n(O) n(O_3) = k_2 n(M) n(O_2) n(O) \quad (6)$$

which lead to

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1 n(M) n^2(O) + 2k_3 n(O_3) n(O)$$
$$= 2n(O_2) J_2 \quad (7)$$

In the stratosphere, reaction (1) takes place very slowly and can be omitted in all photochemical discussions of stratospheric ozone. Furthermore, atomic oxygen is always in photochemical equilibrium with ozone. Therefore the rate of change of $n(O_3)$ in a pure oxygen stratosphere becomes

$$\frac{dn(O_3)}{dt} + \frac{2k_3 J_3}{k_2 n(M) n(O_2)} n^2(O_3) = 2n(O_2) J_2 \quad (8)$$

Introducing the time $\tau_q(O_3)$ necessary to attain 50% (or to reach 80% from 50%) of the photochemical abundance $n_*(O_3)$, we obtain

$$\tau_{eq}(O_3) = 0.275 n_*(O_3)/n(O_2) J_2 \quad (9)$$

With numerical values it can be shown [*Nicolet*, 1974] (Figure 1) that photochemical equilibrium can be adopted for $n(O_3)$ at the stratopause. From (8), the equation

$$n_*^2(O_3) = (k_2/k_3) n(M) n^2(O_2) (J_2/J_3) \quad (10)$$

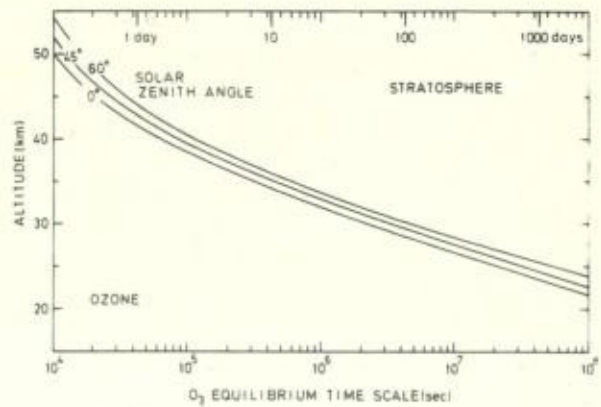represents photochemical equilibrium conditions in the upper

Fig. 1. Equilibrium time scales for ozone in a pure oxygen atmosphere: less than 1 day above 45 km, more than 1 year below 25 km for daytime conditions.

stratosphere for a pure oxygen atmosphere. From this preliminary analysis it can be concluded that there are important differences between the upper and lower stratospheres. At and immediately below the stratopause the time required to reach photochemical conditions is less than one day; at 20 km with an equilibrium time of several years, a complete departure from photochemical equilibrium conditions, and even from steady state conditions that include a transport term, must be considered. Nevertheless, it is not possible to reach an agreement between the calculated values under photo-equilibrium conditions, even at the stratopause, and the observed values [*Krueger*, 1973] when the ozone problem is considered in a pure oxygen atmosphere. It can be shown [*Nicolet*, 1974] (Figure 2) that the observed concentrations are less than the calculated values and that there is no possibility to modify the numerical parameters: k_2 and k_3 are well-known, $n(M)$ and $n(O_2)$ are atmospheric concentrations, J_2 cannot be wrong by more than 30%, and J_3 is sufficiently well-known. An aeronomic possibility is that the increase of the effective value of J_3 is due to various actions of HO_x, NO_x, and ClO_x.

REACTIONS IN A HYDROGEN-OXYGEN ATMOSPHERE

A hydrogen-oxygen atmosphere seems to be very complicated [*Bates and Nicolet*, 1950*c*]. However, when an analysis of the various reaction rates is made, a certain number of them can be ignored, and for several years it was assumed [e.g.,
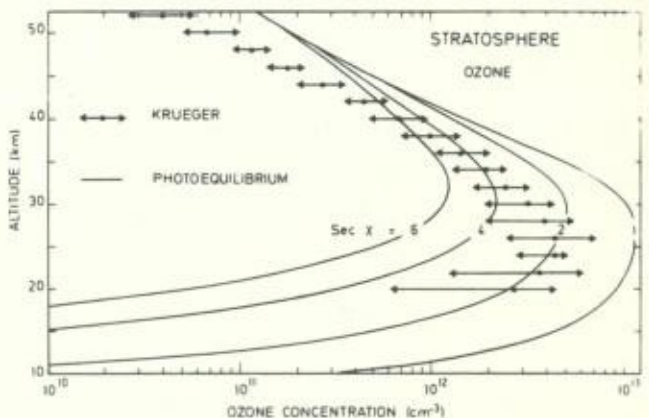

Fig. 2. Observed and calculated ozone profiles. Calculation for photoequilibrium conditions at various solar zenith angles χ, sec $\chi = 1, 2, 4,$ and 6. Range in ozone observations of 24 rocket flights between 58°S and 64°N by *Krueger* [1973].

Hunt, 1966; *Leovy*, 1969] that the reactions of OH and HO_2 radicals with O and O_3 were the essential reactions explaining the aeronomic behavior of stratospheric ozone.

The reactions involving only a single hydrogen atom (free or combined) and one of the allotropic forms of oxygen are as follows: A three-body reaction involving atomic hydrogen leads to a hydroperoxyl radical:
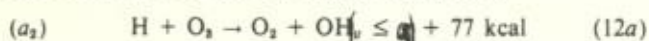
(a_1) $H + O_2 + M \rightarrow HO_2 + M + 46$ kcal   (11a)

which has the rate coefficient

$$a_1 = 2.1 \times 10^{-32} e^{290/T} \qquad (11b)$$

corresponding to an average value of two laboratory determinations [*Kurylo*, 1972; *Wong and Davis*, 1974; *Davis*, 1974].

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

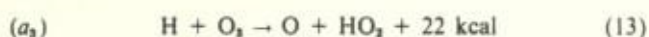(a_2) $H + O_3 \rightarrow O_2 + OH_{v \leq 9} + 77$ kcal   (12a)

A new value for the rate coefficient has recently been deduced (M. A. A. Clyne and P. B. Monkhouse, private communication, 1975); it is

$$a_2 = 1.2 \times 10^{-10} e^{-560/T} \text{ cm}^3 \text{ s}^{-1} \qquad (12b)$$

leading to 1.5×10^{-11} cm^3 s^{-1} at the stratopause.

The production of hydroperoxyl radicals by

(a_3) $H + O_2 \rightarrow O + HO_2 + 22$ kcal   (13)

with a rate coefficient a_3 that has not been measured, and by a three-body association process

(a_4) $OH + O + M \rightarrow M = HO_2 + 63$ kcal   (14)

with a conventional value of the three-body rate coefficient a_4, is neglected in comparison with that of reaction (11).

An important reaction in the mesosphere and in the upper stratosphere is the bimolecular process

(a_5) $OH + O \rightarrow H + O_2 + 17$ kcal   (15a)
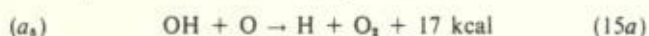
Laboratory data [*Clyne and Thrush*, 1963; *Kaufman*, 1964, 1969; *Breen and Glass*, 1970; *Westenberg et al.*, 1970] indicate possible values between 2 and 7×10^{-11} cm^3 s^{-1}. A value such as

$$a_5 = (4 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (15b)$$

may be considered as a working value with a possible error of $\pm 50\%$.

It is clear that if the effects of (15) are important in the mesosphere and at the stratopause, they become negligible in the lower stratosphere where other processes involving ozone can play a role. The chain reaction involving hydroxyl radicals and ozone introduced by *McGrath and Norrish* [1958], which has been used and rejected several times due to the lack or imprecision of experimental data, can now be considered, since sufficiently precise values of the rate coefficients have been obtained.

The reactions

(a_6) $OH + O_3 \rightarrow HO_2 + O_2 + 39$ kcal   (16a)

and

(a_{6c}) $HO_2 + O_3 \rightarrow OH + 2O_2 + 31$ kcal   (16b)
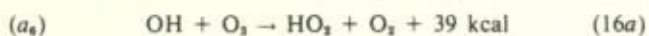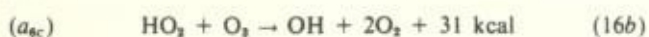
must be finally considered. Very recent measurements have been reported [*Anderson and Kaufman*, 1973; *DeMore*, 1973;

*Simonaitis and Heicklen*, 1973a; *Davis*, 1974] for a_6. A value such as

$$a_6 = 1.6 \times 10^{-12} e^{-1000/T} \text{ cm}^3 \text{ s}^{-1} \qquad (16c)$$

leads to 5.5×10^{-14} cm^3 s^{-1} at room temperature [*Anderson and Kaufman*, 1973] and to $1-2 \times 10^{-14}$ cm^3 s^{-1} at temperatures of the lower stratosphere. Such values are less (by more than a factor of 10) than the values which were used during several years in the aeronomic study of the lower stratosphere. The rate coefficient of (16b) is not yet precise; however, it is possible to deduce a working value, and

$$a_{6c} = 1 \times 10^{-13} e^{-1250/T} \text{ cm}^3 \text{ s}^{-1} \qquad (16d)$$

may be considered as an acceptable average value between the values obtained by *Simonaitis and Heicklen* [1973c] and *DeMore and Tschuikow-Roux* [1974]. Such a value of the rate coefficient leads to 3×10^{-16} cm^3 s^{-1} in the lower stratosphere, i.e., a very low value.

The principal reaction leading to OH in the upper stratosphere involves atomic oxygen [*Kaufman*, 1964], for which there is no laboratory measurement:

(a_7) $O + HO_2 \rightarrow O_2 + OH_{v \leq 6} + 55$ kcal   (17a)
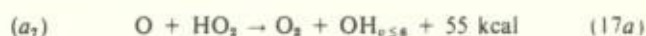
Reactions (15) and (17) must be compared since they represent at the stratopause level the chain reaction which is involved in the ozone-destroying mechanism through the direct attack of oxygen atoms and reformation of oxygen molecules. There is no way to substantiate any value of the rate coefficient between 1 and 7×10^{-11} cm^3 s^{-1}, and we write

$$a_7 = 1-7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (17b)$$

even if experimental results [*Hochanadel et al.*, 1972] have been simulated using the highest value. It must be pointed out here that experimental data are urgently needed in order to determine the exact ratio a_5/a_7, which must be known in order to calculate precisely the effect of these radicals on the ozone concentration at the stratopause level.

In addition to these various collision processes, the possibility of photodissociation of the hydroxyl and hydroperoxyl radicals may be considered:

(a_8) $OH + h\nu \rightarrow O + H$ (18)
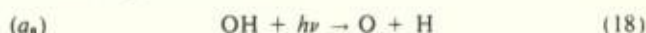
Such a reaction will be ignored ($a_8 = 0$) even if there is a possibility of a dissociation owing to the predissociation of the $A^2\Sigma^+$ state for levels $v' > 0$.

The absorption of HO_2 has been observed [*Hochanadel et al.*, 1972; *Paukert and Johnston*, 1972] and should lead to

(a_9) $HO_2 + h\nu \rightarrow OH + O$ (19)
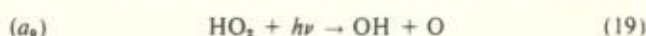
It is certain that the photodissociation process (19) is less important than reaction (17) in the upper stratosphere.

As for the photodissociation process

(a_{10}) $HO_2 + h\nu \rightarrow H + O_2$ (20)
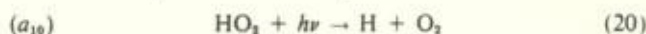
in which the bonds between H and O atoms are difficult to break, it can be ignored, and $a_{10} = 0$.

Expressions for the equilibrium ratios of $n(OH)/n(H)$ and $n(HO_2)/n(H)$ (Figure 3) can be easily obtained for the stratopause level and the upper stratosphere, since only a limited number of reactions is involved. Thus

$$\frac{n(OH)}{n(H)} = \frac{a_1 n(M) n(O_2) + a_2 n(O_3)}{a_5 n(O)} \qquad (21)$$

$$\frac{n(HO_2)}{n(H)} = \frac{a_1 n(M) n(O_2)}{a_7 n(O)} \qquad (22)$$

and

$$\frac{n(OH)}{n(HO_2)} = \frac{a_1 n(M) n(O_2) + a_2 n(O_3)}{a_1 n(M) n(O_2)} \cdot \frac{a_7}{a_5} \qquad (23)$$

The conventional equation (10) for equilibrium conditions at the stratopause for a pure oxygen atmosphere becomes, in a hydrogen-oxygen atmosphere,

$$n^2(O_3) = \frac{k_2}{k_3} n(M) n^2(O_2) \frac{J_3}{J_2(1 + A)} \qquad (24)$$

with the correction term

$$A = \frac{a_5 n(OH) + a_7 n(HO_2)}{2 k_3 n(O_3)} \qquad (25)$$

The correction term (25) shows clearly that it is difficult to make an exact numerical application of the effect of hydroxyl and hydroperoxyl radicals on the ozone concentration in the upper stratosphere and lower mesosphere. All applications which have been made lead to equivocal deductions. The only possible conclusion is that a controlling effect by the hydroxyl and hydroperoxyl radicals on the ozone concentration at the stratopause level requires that their concentrations be of the order of 10^7 cm^{-3}.

In the lower stratosphere, the conventional equation (8) must be replaced by

$$\frac{dn(O_3)}{dt} + n(O_3)[2 k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2)]$$

$$= 2 n(O_2) J_2 \qquad (26)$$

where the term $2 k_3 n(O)$ is very small. In a hydrogen-oxygen atmosphere the ratio $n(OH)/n(HO_2)$ in the lower stratosphere would be

$$\frac{n(OH)}{n(HO_2)} = \frac{a_{6c}}{a_6} = \frac{(3 \pm 1) \times 10^{-16}}{(1.5 \pm 0.5) \times 10^{-14}} = \frac{1}{50} \qquad (27)$$

at a temperature of the order of 210 ± 10 K.

With a negligible production of ozone at this level (with no transport involved), a reduction in 2 months of the ozone concentration to 50% of its initial value requires at least 5×10^6 OH molecules cm^{-3} or 3×10^8 HO$_2$ molecules cm^{-3}. A special study is required, therefore, to determine with precision the various processes involved, including the simultaneous production in the lower stratosphere of OH and HO$_2$ radicals, their related reactions, and their final destruction.

The production of hydroxyl radicals in the stratosphere must result first from a dissociation process of water vapor.
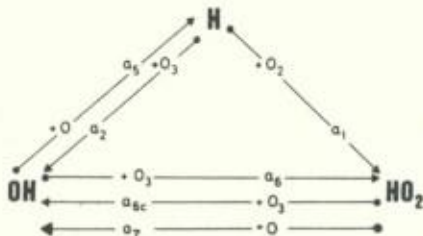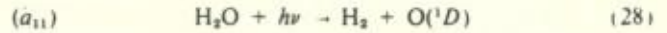

Fig. 3. Reaction scheme of H, OH, and HO$_2$ showing their interconnection at the stratopause.

The photodissociation of H$_2$O which leads to

(a_{11}) $\qquad$ H$_2$O + $h\nu$ $\to$ H$_2$ + O(^{1}D) $\qquad$ (28)

is a mesospheric process above 70 km due to the effect of solar Lyman α at 121.6 nm. If an effect on H$_2$O caused by oxygen atoms in their normal state ^3P has not been detected because the reaction was endothermic, an important process will occur with oxygen atoms in their first excited state, ^1D [Engleman 1965]:

(a_{12}) O(^{1}D) + H$_2$O $\to$ OH + OH*($v \leq 2$) + 29 kcal $\quad$ (29a)
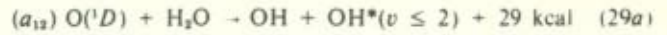
for which a relatively precise value can be adopted

$$a_{12} = a_{12}^* = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (29b)$$

if we adopt the most recent experimental values [Heidner et al 1973; Cvetanovic, 1974]. With the O(^{1}D) concentrations which exist in the stratosphere there is permanent (daytime) production of OH radicals.

However, unpublished measurements (H. I. Schiff, private communication, 1975) indicate that a_{12}^* is only of the order of 2×10^{-10} cm^3 s^{-1} at room temperature and has a negative activation energy leading to about

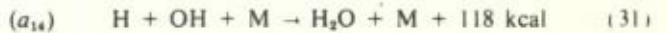$$a_{12}^* = 8 \times 10^{-11} e^{288/T} \text{ cm}^3 \text{ s}^{-1} \qquad (29c)$$

The normal photodissociation process

(a_{13}) $\qquad$ H$_2$O + $h\nu$ $\to$ H(^{2}S) + OH($X^2\Pi$) $\qquad$ (30)
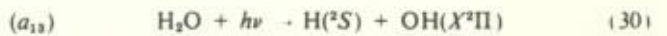
which can still occur in the stratosphere, is less important than the reaction process (29).

Finally, when dissociation of water vapor proceeds through (29), its re-formation may occur through

(a_{14}) $\qquad$ H + OH + M $\to$ H$_2$O + M + 118 kcal $\qquad$ (31)

which can be neglected, as contrasted with the treatment in other possible aeronomic processes, such as a_{16} and a_{17}.

The reaction of hydrogen atoms and hydroperoxyl radicals leads to two hydroxyl radicals:

(a_{15}) $\qquad$ H + HO$_2$ $\to$ OH + OH$_{v \leq 4}$* + 39 kcal $\qquad$ (32)
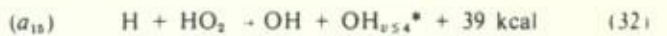
This reaction has been observed [Cashion and Polanyi, 1959], but it is not yet possible to find a precise value for its rate coefficient. A review by Lloyd [1974] and a discussion by Kaufman [1974] on rate coefficients a_{15}, a_{20}, and a_{22} and their ratios indicate the difficulty in adopting correct values.
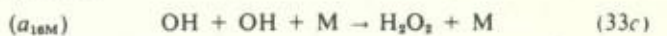
The reaction between two hydroxyl radicals leads to the re-formation of water vapor:

(a_{16}) $\qquad$ OH + OH $\to$ H$_2$O + O + 17 kcal $\qquad$ (33a)
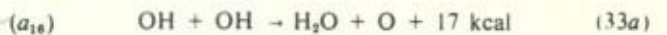
If recent laboratory measurements [Westenberg and de Haas, 1973a; Trainor and von Rosenberg, 1974a; Clyne and Down, 1974] are considered, $T = 300$ K, the following value is adopted:

$$a_{16} = 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \qquad (33b)$$

In addition to the two-body process (33), the three-body association

(a_{16M}) $\qquad$ OH + OH + M $\to$ H$_2$O$_2$ + M $\qquad$ (33c)

must be introduced with the rate coefficient [Trainor and von Rosenberg, 1974a]

$$a_{16M} = 2.5 \times 10^{-31} n(M) \text{ cm}^3 \text{ s}^{-1} \qquad (33d)$$

In the same way, the reaction between hydroxyl and hydroperoxyl radicals leads to H_2O:

(a_{17}) $OH + HO_2 \rightarrow H_2O + O_2 + 72$ kcal   (34)
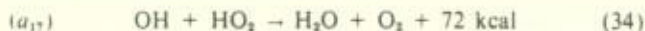
Laboratory results by *Hochanadel et al.* [1972] lead to a very high value of the rate coefficient

$$a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (35)$$

This value should be acceptable, since another analysis [*DeMore and Tschuikow-Roux*, 1974] results in 1.6×10^{-10}, believed to be accurate to within a factor of 3. Under these conditions the reaction between OH and HO_2 becomes the most important cause of re-formation of water vapor in the stratosphere. However, if a much lower value is used, as was suggested by *Kaufman* [1974] and given by *Hack et al.* [1975], the determination of the $OH + HO_2$ concentration remains an unresolved problem.

Other reactions can lead to the formation of H_2O, but they are not as important in the stratosphere as the reactions that lead to its re-formation. The three-body association

(a_{18}) $H_2 + O + M \rightarrow H_2O + 116$ kcal   (36)
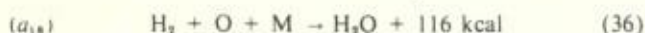
should have a small rate coefficient, since it is spin-forbidden when normal oxygen atoms are involved and is therefore neglected.

The exothermic reaction between H_2 and OH

(a_{19}) $H_2 + OH \rightarrow H_2O + H + 15$ kcal   (37a)
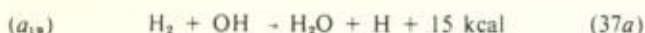
requires a relatively high activation energy [*Greiner*, 1969]. A recent laboratory measurement [*Smith and Zellner*, 1974] between 210 and 410 K results in

$$a_{19} = 1.8 \times 10^{-11} e^{-2320/T} \text{ cm}^3 \text{ s}^{-1} \quad (37b)$$

This reaction may be introduced into the aeronomic chemistry of molecular hydrogen.

Finally, in addition to (32), the reaction between hydrogen atoms and hydroperoxyl radicals may lead to the re-formation of H_2O:

(a_{20}) $H + HO_2 \rightarrow H_2O + O + 55$ kcal   (38)
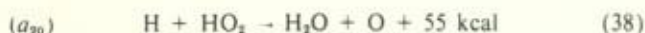
The rate coefficient a_{20} should be of the same order of magnitude as a_{18}, but no acceptable value has been found. This reaction is neglected in the formation of stratospheric water vapor but is related to the formation of H_2 (see (a_{23})).

According to the preceding analysis of the dissociation and re-formation of the water vapor in the stratosphere, it is clear that the dissociation of water vapor leads to the following equation for equilibrium in a pure oxygen-hydrogen atmosphere:

$$n(H_2O)a^*n(O^*) = a_{20}n(H)n(HO_2)$$
$$+ n(OH)[a_{16}n(OH) + a_{17}n(HO_2) + a_{19}n(H_2)] \quad (39a)$$

This equation corresponds, in the first approximation, to

$$n(H_2O)a_{12}^*n(O^*) = a_{17}n(HO_2)n(OH) \quad (39b)$$

where $n(O^*)$ is the concentration of excited oxygen atoms. However, we must take into account the effect of H_2 and CH_4 in the production of OH radicals and also the reaction processes resulting from the presence of H_2O_2, CH_4, and HNO_3.

The final equation will be

$$n(OH)\left[a_{16}n(OH) + a_{17}n(HO_2) + a_{20}n(H_2O_2) \right.$$
$$+ c_2\left(\frac{1-X}{2}\right)n(CH_4) + b_{27}n(HNO_3) \right]$$
$$= a_{-}^{*}n(O^*)\left[n(H_2O) + n(H_2) + \frac{1+X}{2}n(CH_4) \right] \quad (40)$$

To obtain this equation it is necessary to study the reactions involving nitrogen oxides and methane. But, in the discussion concerning the more important reactions of hydroxyl and hydroperoxyl radicals the reactions involving HO_2 and H_2 must be considered.

Molecular hydrogen, which is a permanent constituent of the troposphere (0.5 ppm), cannot be completely neglected in the stratosphere, and its observation may lead to the understanding of stratospheric aeronomic process. It is formed by a three-body association of two hydrogen atoms

(a_{21}) $H + H + M \rightarrow H_2 + M + 103$ kcal   (41)
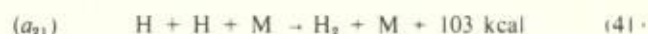
which can be neglected, as is not the case with bimolecular processes.

The reaction

(a_{22}) $H + OH \rightarrow H_2 + O + 2$ kcal   (42a)
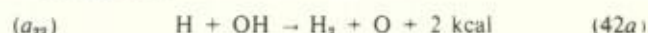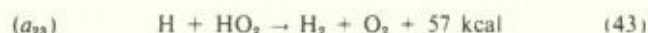
requires a high activation energy [*Baulch et al.*, 1972]

$$a_{22} = 1.4 \times 10^{-14} Te^{-3500/T} \text{ cm}^3 \text{ s}^{-1} \quad (42b)$$

In fact, a more important mode of molecular hydrogen formation occurs through the reaction of hydrogen atoms with hydroperoxyl radicals

(a_{23}) $H + HO_2 \rightarrow H_2 + O_2 + 57$ kcal   (43)

for which a precise coefficient is not available. This reaction, which occurs with a_{18} and a_{20}, has an important role in the mesosphere; it can produce molecular hydrogen, which may be transported downward into the stratosphere.
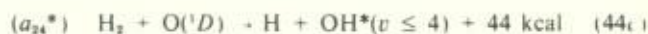
The destruction process

(a_{24}) $H_2 + O \rightarrow OH + H - 2$ kcal   (44a)
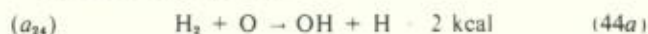
which is endothermic by about 1.9 kcal, cannot be neglected above 100 km, where the temperature is relatively high. Its rate coefficient recommended by *Baulch et al.* [1972] is

$$a_{24} = 3.0 \times 10^{-14} Te^{-4480/T} \text{ cm}^3 \text{ s}^{-1} \quad (44b)$$

In fact the process which attacks molecular hydrogen in the stratosphere is the reaction

(a_{24}^*) $H_2 + O(^1D) \rightarrow H + OH^*(v \leq 4) + 44$ kcal   (44c)

with a rate coefficient that is assumed to be equal (for the purpose of aeronomic calculations in the stratosphere) to a_{12}^* [*Cvetanovic*, 1974; *Heidner and Husain*, 1973], i.e.,

$$a_{24}^* = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (44d)$$

However, more recent measurements (H. I. Schiff, personal communication, 1975) indicate that a_{24}^* is only about 1.3×10^{-10} cm^3 s^{-1} at room temperature and has an activation energy which leads to about

$$a_{24}^* = 5 \times 10^{-10} e^{-400/T} \text{ cm}^3 \text{ s}^{-1} \quad (44e)$$

Thus a_{24}^* decreases with temperature when a_{12}^* increases.

Considering the numerical values of the various coefficients, the chemical conditions for molecular hydrogen are written, to a good approximation, as

$$\frac{dn(H_2)}{dt} + n(H_2)[a_{24}*n(O^*) + a_{19}n(OH)]$$

$$= n(H)n(HO_2)a_{23} \qquad (45)$$

The H_2 destruction processes occur in the stratosphere while H_2 production is particularly important in the upper mesosphere. Since loss processes are very slow, the chemical equation must be written

$$\frac{\partial n(H_2)}{\partial t} + \frac{\partial [n(H_2)w]}{\partial z} + n(H_2)[a_{24}*n(O^*) + a_{19}n(OH)]$$

$$= n(H)n(HO_2)a_{23} \qquad (46)$$

where w is the diffusion velocity. Stratospheric H_2 depends not only on its concentration in the troposphere (the lower boundary condition) and upward vertical transport, but also on possible downward transport from the mesosphere, where there is a production source. Also, H_2 can be produced by reactions involving CH_4, as will be shown in the analysis of stratospheric methane.

The photodissociation of molecular hydrogen

(a_{25}) $\qquad\qquad H_2 + h\nu \rightarrow H + H$
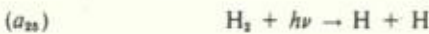
does not occur below 100 km and is therefore neglected.

Finally, various reactions with nitrogen oxides in which H, OH, and HO_2 are involved, which can modify the picture of a hydrogen-oxygen atmosphere, will be introduced in another section. However, a reaction such as

(a_{26}) $\qquad\qquad HO_2 + NO \rightarrow OH + NO_2$
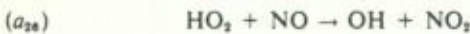
in the stratosphere should be kept in mind before reaching any final conclusion; it will be considered as reaction (b_{29}), equation (129).

In the foregoing discussion, hydrogen peroxide was not considered, and its reactions were not listed. However, it is produced by a two-body process

(a_{27}) $\qquad HO_2 + HO_2 \rightarrow H_2O_2 + O_2 + 42$ kcal $\qquad (47a)$
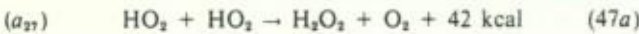
with a rate coefficient which does not require a high activation energy [Foner and Hudson, 1962]. Recent values of the rate coefficients at room temperature are

$$a_{27} = (9.5 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \qquad (47b)$$

according to Hochanadel et al. [1972], or

$$a_{27} = (3.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \qquad (47c)$$
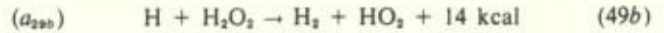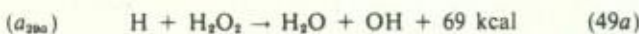
according to Paukert and Johnston [1972]. More experimental data are needed before the correct evaluation of the various effects of these important reactions can be obtained.

The photodissociation of H_2O_2 is known from laboratory measurements, and the essential process in the stratosphere is

(a_{28}) $\qquad\qquad H_2O_2 + h\nu \rightarrow 2OH \qquad (48)$
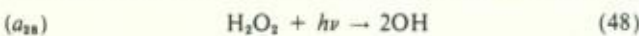
The variation of the photodissociation coefficient $J_{H_2O_2}$ with the solar angle is particularly important in the lower stratosphere, where its value decreases to $10^{-6} \leq J_{H_2O_2} < 10^{-5}$ s^{-1}.

The reaction with atomic hydrogen leads to

(a_{29a}) $\qquad H + H_2O_2 \rightarrow H_2O + OH + 69$ kcal $\qquad (49a)$

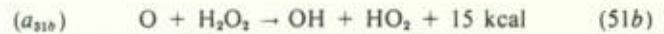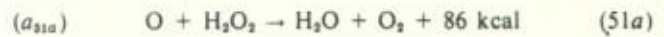(a_{29b}) $\qquad H + H_2O_2 \rightarrow H_2 + HO_2 + 14$ kcal $\qquad (49b)$

Experimental evidence [Klemm et al., 1975; Gorse and Volman, 1974] indicates that the role of (49) in the stratosphere is not important. But the reaction between a hydroxyl radical and hydrogen peroxide

(a_{30}) $\qquad OH + H_2O_2 \rightarrow H_2O + HO_2 + 30$ kcal $\qquad (50a)$
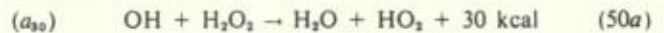
is important, since its rate coefficient is of the order of 1×10^{-12} cm^{-3} s^{-1} at 298 K with an activation energy of the order of 1.2 kcal/mol. According to various laboratory determinations [Greiner, 1968; Gorse and Volman, 1972; Hack et al., 1975], the following value can be used

$$a_{30} = 8 \times 10^{-12} e^{-600/T} \text{ cm}^3 \text{ s}^{-1} \qquad (50b)$$

and will result in a rate of about 5×10^{-13} cm^3 s^{-1} in the lower stratosphere. Finally, the reaction between oxygen atoms and hydrogen peroxide molecules will be considered, since atomic oxygen is an important minor constituent of the stratosphere:

(a_{31a}) $\qquad O + H_2O_2 \rightarrow H_2O + O_2 + 86$ kcal $\qquad (51a)$

(a_{31b}) $\qquad O + H_2O_2 \rightarrow OH + HO_2 + 15$ kcal $\qquad (51b)$

The total rate coefficient obtained in a recent publication [Davis et al., 1974b] is

$$a_{31} = 2.75 \times 10^{-12} e^{-2125/T} \text{ cm}^3 \text{ s}^{-1} \qquad (51c)$$

leading to a value of about 1×10^{-16} cm^3 s^{-1} in the lower stratosphere, i.e., much smaller than (a_{30}), which is the principal stratospheric reaction with the photodissociation process of H_2O_2.

Experimental evidence does not rule out $O(^1D)$-H_2O_2 reactions such as

$(a_{31}*)$ $\qquad O(^1D) + H_2O_2 \rightarrow OH + O_2 + 60$ kcal $\qquad (51d)$
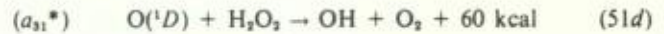
with a rate coefficient of the order of 10^{-10} cm^3 s^{-1}. However, like (51a), it is a very slow loss process of hydrogen peroxide.

Hydrogen peroxide could react with nitrogen oxides; for example,

(a_{32}) $\qquad NO + H_2O_2 \rightarrow HNO_2 + OH + 11$ kcal $\qquad (52)$
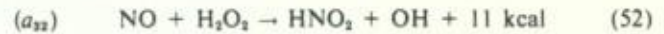
This reaction is negligible (see reaction (b_{30})) like

(a_{33}) $\qquad NO_2 + H_2O_2 \rightarrow HNO_3 + OH + 4$ kcal $\qquad (53)$
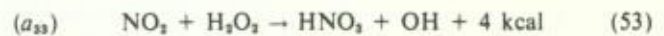
which is not used in stratospheric aeronomy [Gray et al., 1972].

Various rapid reactions such as

(a_{34}) $\qquad H + NO_2 \rightarrow OH + NO + 30$ kcal $\qquad (54)$
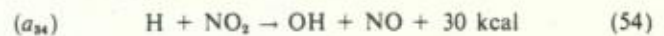
can be neglected, since other reactions (here $H + O_2 \rightarrow OH + O_2$) are always more important. However, two reactions with carbon monoxide must be considered. The first

(a_{35}) $\qquad HO_2 + CO \rightarrow CO_2 + OH + 64$ kcal $\qquad (55)$
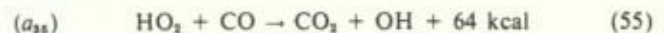
however, is without importance, since $a_{35} < 10^{-20}$ cm^3 s^{-1} [Simonaitis and Heicklen, 1973b; Davis et al., 1973c]. As far as the reaction of CO with OH is concerned,

(a_{36}) $\qquad OH + CO \rightarrow CO_2 + H + 24$ kcal $\qquad (56a)$
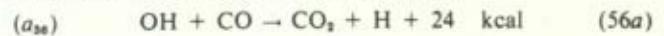
can play a role in the lower stratosphere, since its rate coefficient [Greiner, 1969; Smith and Zellner, 1973; Westenberg and de Haas, 1973b; Davis et al., 1973a; Trainor and von Rosenberg, 1974b] is
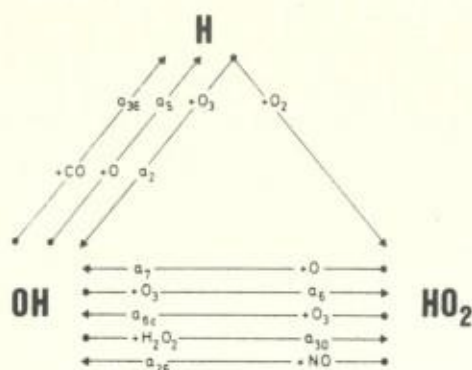
Fig. 4. Partial reaction scheme of H, OH, and HO_2 indicating the complexity of their interactions, particularly in the lower stratosphere.

$$a_{36} = (1.25 \pm 0.25) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad (56b)$$

in the lower stratosphere. The limiting value would be, according to *Sie et al.* [1975a],

$$a_{36M=} = 3.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad (56c)$$

If only important reactions (Figure 4) from a_1 to a_{36} are considered with photoequilibrium conditions, which can be applied to H and OH in the stratosphere, the important ratio $n(OH)/n(HO_2)$ can be written:

$$n(HO_2)[a_{6c}n(O_3) + a_7n(O) + a_{17}n(OH)$$
$$+ 2a_{27}n(HO_2) + a_{26}n(NO)]$$
$$= n(OH)[a_5n(O) + a_6n(O_3) + a_{19}n(H_2)$$
$$+ a_{30}n(H_2O_2) + a_{36}n(CO)] \quad (57)$$

With the aim of illustrating the day equilibrium represented by (57), two figures have been prepared. In Figure 5 the various percentages of the different coefficients affecting $n(OH)$ are given [*Nicolet*, 1974]. In the upper troposphere and lower stratosphere the dominant path transforming OH to H → HO_2 is the reaction with CO. It is therefore necessary to know the exact concentration and vertical distribution of carbon monoxide in the lower stratosphere. In the lower and middle stratosphere the reaction of OH with O_3 plays the leading role. At the stratopause and in the upper stratosphere the reaction with atomic oxygen transforming OH to H + HO_2 becomes the principal process. The effect of H_2 and also of H_2CO and CH_4 (not shown here) may be neglected, although they can play a role in the lower troposphere.

As far as HO_2 is concerned, it can be seen in Figure 6 that, in the lower stratosphere, the reactions with nitric oxide cannot be neglected. The exact role of NO depends on the absolute value of the rate coefficient, which is not yet well-known, and also on the vertical distribution of its concentration, which is extremely variable in the lower stratosphere, particularly when the variations of the tropopause level are important. As for OH, the effects of the reactions of HO_2 with O_3 and O occur in the middle and upper stratosphere, respectively. At 30 km, there is a simultaneous effect of about 30% of the reactions with OH, HO_2, and O. Thus the main features of Figures 5 and 6 correspond to the effect on OH and HO_2 of atomic oxygen at the stratopause and in the upper stratosphere and to the effect of O_3 in the middle stratosphere and also in the lower stratosphere, where the action of carbon monoxide and nitric oxide becomes extremely important. The essential features of the ratio $n(OH)/n(HO_2)$ appear very sensitive in the lower

stratosphere to the absolute values of the CO and NO concentrations, and the behavior of OH and HO_2, which affects all chemical processes below 20 km, requires an exact knowledge of their rate coefficients with nitrogen oxides. Thus equation (23) can be adopted as the upper boundary daytime condition at the stratopause level

$$\frac{n(OH)}{n(HO_2)} = \frac{a_1 n(M)n(O_2) + a_2 n(O_3)}{a_1 n(M)n(O_2)} \cdot \frac{a_7}{a_5} \quad (58)$$

In the lower stratosphere for daytime conditions, we have

$$\frac{n(OH)}{n(HO_2)} = \frac{a_{6c}n(O_3) + a_{26}n(NO)}{a_6 n(O_3) + a_{36}n(CO)} \quad (59)$$

and, for a low tropopause,

$$\frac{n(OH)}{n(HO_2)} = \frac{a_{26}n(NO)}{a_{36}n(CO)} \quad (60)$$

Thus aeronomic behavior must be discussed with special attention being given to the lower stratosphere in order to determine how ozone can be affected by the variation of the $n(OH)/n(HO_2)$ ratio. The absolute values of the OH and HO_2 concentrations must be determined to establish quantitative effects (equation (26)). Before final conclusions can be reached, laboratory measurements are needed on various reactions such as OH + HO_2 (a_{17}), HO_2 + HO_2 (a_{27}), O + HO_2 (a_7), NO + HO_2 (a_{26}), and H + HO_2 ((a_{18}), (a_{20}), and (a_{23})) in order to determine their rate coefficients with accuracy.

REACTIONS AFTER OXIDATION OF METHANE

Methane, which is mixed in the troposphere, is photodissociated in the mesosphere and is dissociated by oxidation processes in the stratosphere.

Atomic oxygen attacks methane [see, for example, *Nicolet*, 1974] through

$$(c_1) \qquad O(^3P) + CH_4 \rightarrow CH_3 + OH - 2 \text{ kcal} \quad (61a)$$
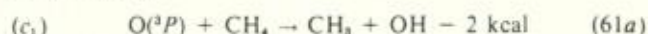
which, endothermic by about 2 kcal, is a slow reaction. Its rate coefficient, which is not known with precision, is only about [*Westenberg and de Haas*, 1969]

$$c_1 = 3.3 \times 10^{-11} e^{-4800/T} \text{ cm}^3 \text{ s}^{-1} \quad (61b)$$

But, in the stratosphere, the reaction of CH_4 with atomic oxygen in the electronically excited ^1D state is rapid; it leads to

$$(c_{1a}^*) \qquad O(^1D) + CH_4 \rightarrow CH_3 + OH + 44 \text{ kcal} \quad (61c)$$
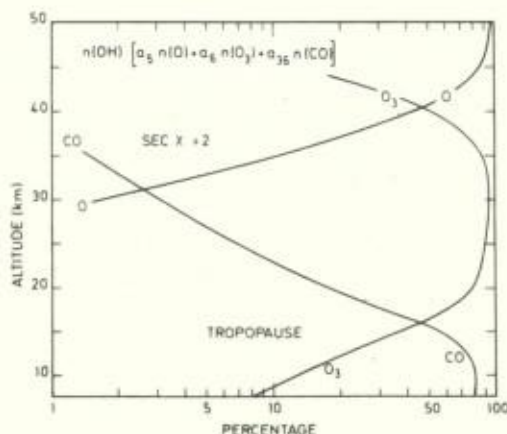
Fig. 5. Profiles (percentages) of various terms affecting OH in the determination of the ratio $n(HO_2)/n(OH)$, to be considered as examples.

Fig. 6. Profiles (percentages) of various terms affecting HO_2 in the determination of the ratio $n(HO_2)/n(OH)$, to be considered as examples.

and also

(c_{1b}^*) $\qquad$ $O(^1D) + CH_4 \rightarrow H_2 + H_2CO$ $\qquad$ $(61d)$

which occurs to the extent of 9% [*Lin and DeMore*, 1973b]. The total rate coefficient for $O(^1D)$ [*Greenberg and Heicklen*, 1972; *Heidner and Husain*, 1973; *Cvetanovic*, 1974] is

$$c_1^* = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (61e)$$

almost identical to the reactions of $O(^1D)$ with H_2 and H_2O.

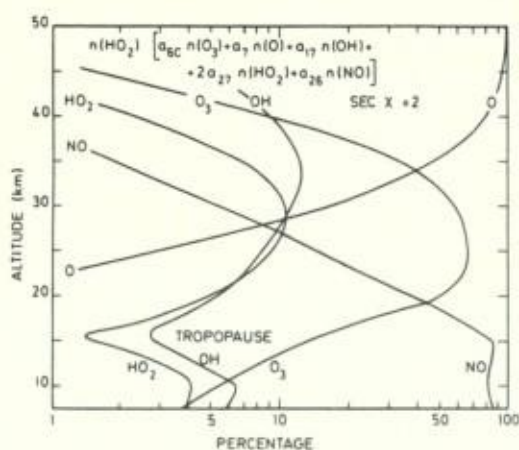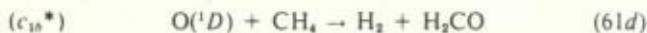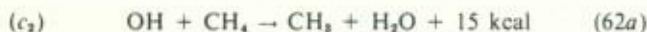However, unpublished measurements (H. I. Schiff, private communication, 1975) indicate that c_1^* is only about $1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at room temperature and is not therefore identical to a_{12}^* and a_{24}^*.

The other important reaction in the stratosphere is

(c_2) $\qquad$ $OH + CH_4 \rightarrow CH_3 + H_2O + 15 \text{ kcal}$ $\qquad$ $(62a)$
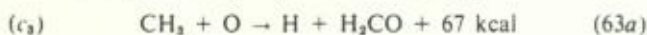
with a well-defined rate coefficient

$$c_2 = 3.5 \times 10^{-12} e^{-1800/T} \text{ cm}^3 \text{ s}^{-1} \qquad (62b)$$

based on laboratory measurements by *Greiner* [1970], *Davis et al.* [1973a], and *Margitan et al.* [1974], which leads to a value of $4 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 200 K in the lower stratosphere.

Methyl radicals, which are produced by oxidation processes of CH_4, may react rapidly with atomic oxygen

(c_3) $\qquad$ $CH_3 + O \rightarrow H + H_2CO + 67 \text{ kcal}$ $\qquad$ $(63a)$

with a rate coefficient [*Slagle et al.*, 1974; *Washida and Bayes*, 1973]

$$c_3 = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (63b)$$

This reaction should be important in the mesosphere, but in the stratosphere, methyl radicals react by a three-body process with molecular oxygen:
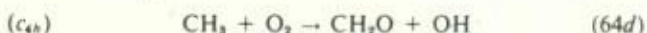
(c_{4a}) $\qquad$ $CH_3 + O_2 + M \rightarrow CH_3O_2 + M + 26 \text{ kcal}$ $\qquad$ $(64a)$
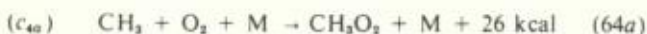
The rate coefficient with $M = N_2$ is [*Basco et al.*, 1972]

$$c_{4a} = 2.6 \times 10^{-31} n(N_2) \text{ cm}^3 \text{ s}^{-1} \qquad (64b)$$

with a limiting value

$$c_{4a\infty} = 4.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \qquad (64c)$$

The following reaction must also be considered:

(c_{4b}) $\qquad$ $CH_3 + O_2 \rightarrow CH_2O + OH$ $\qquad$ $(64d)$

where the rate coefficient is (N. Washida and K. Bayes, private communication, 1975)
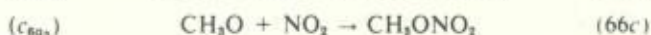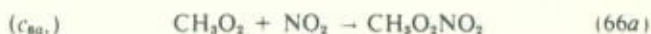
$$c_{4b} = 6.5 \times 10^{-13} e^{1090/T} \text{ cm}^3 \text{ s}^{-1} \qquad (64e)$$

Methylperoxy radicals react with oxides of nitrogen [*Spicer et al.*, 1973; *Simonaitis and Heicklen*, 1974b; *Levy*, 1973; *Pitts et al.*, 1973; *Pate et al.*, 1974]. The principal process, and perhaps the sole mode of reaction for nitric oxide, is

(c_{5a}) $\qquad$ $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ $\qquad$ (65)

i.e., an oxidation of NO to NO_2. No numerical value is available for the rate coefficient (see *Levy* [1972, 1973], who has adopted $c_{5a} \geq 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$).

CH_3O_2 and CH_3O could react with NO_2 (J. Heicklen, private communication, 1975) to produce HNO_3 and HNO_2, respectively:

(c_{6a_1}) $\qquad$ $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ $\qquad$ $(66a)$

(c_{6a_2}) $\qquad$ $CH_3O_2 + NO_2 \rightarrow H_2CO + HNO_3$ $\qquad$ $(66b)$

(c_{6a_3}) $\qquad$ $CH_3O + NO_2 \rightarrow CH_3ONO_2$ $\qquad$ $(66c)$

(c_{6a_4}) $\qquad$ $CH_3O + NO_2 \rightarrow H_2CO + HNO_2$ $\qquad$ $(66d)$

The ratio $c_{6a_2}/(c_{6a_1} + c_{6a_2})$ would be about 0.25 and $c_{6a_4}/(c_{6a_3} + c_{6a_4}) \simeq 0.08$. A new analysis is required, since it is extremely important to determine the behavior of nitrogen oxides in the lower stratosphere. If $O(^3P) + CH_3O_2 \rightarrow H_2CO + (O_2 + H)$ has a rate coefficient greater than $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (N. Washida and K. D. Bayes, private communication, 1975), it should be added to reactions (c_5) and (c_6).

The photodecomposition of formaldehyde [*McQuigg and Calvert*, 1969; *Calvert et al.*, 1972; *Sperling and Toby*, 1973; T. Osif and J. Heicklen, private communication, 1975] proceeds by radical and molecular paths:

(c_{7a}) $\qquad$ $H_2CO + h\nu \rightarrow HCO + H$ $\qquad$ $(67a)$

and

(c_{7b}) $\qquad$ $H_2CO + h\nu \rightarrow CO + H_2$ $\qquad$ $(67b)$
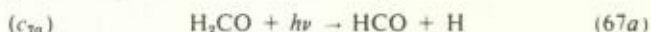
which lead to the production of formyl and carbon monoxide with atomic and molecular hydrogen, respectively. In view of the importance of the production of hydrogen atoms which leads to HO_2 and of the generation of hydrogen molecules in the stratosphere, the relative and absolute importance of the dissociation coefficients J_{HCO-H} and J_{CO-H_2} must be known with precision.

A rapid reaction such as

(c_8) $\qquad$ $OH + H_2CO \rightarrow HCO + H_2O + 36 \text{ kcal}$ $\qquad$ $(68a)$
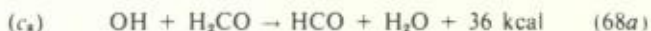
must be also introduced, since [*Morris and Niki*, 1971] its rate coefficient, at 300 K, is

$$c_8 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (68b)$$

The reactions of atomic oxygen and hydrogen with formaldehyde lead also to HCO

(c_9) $\qquad$ $O + H_2CO \rightarrow OH + HCO + 15 \text{ kcal}$ $\qquad$ $(69a)$
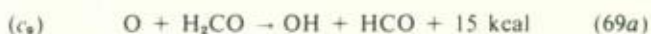
with a rate coefficient [*Herron and Penzhorn*, 1969; *Mack and Thrush*, 1973] at 300 K of

$$c_9 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \qquad (69b)$$

The reaction with atomic hydrogen is still less rapid

(c_{10}) $\qquad$ $H + H_2CO \rightarrow H_2 + HCO + 15 \text{ kcal}$ $\qquad$ $(70a)$

with [*Ridley et al.*, 1972; *Westenberg and de Haas*, 1972a]

$$c_{10} = 2.2 \times 10^{-11} e^{-1880/T} \tag{70b}$$

i.e., $c_{10} = 4-5 \times 10^{-14}$ cm^3 s^{-1} at 297 K. These two reactions, (c_9) and (c_{10}), can be neglected but (c_8) cannot.

The formyl radical is rapidly photodissociated [*Johns et al.*, 1963]

$$(c_{11}) \qquad HCO + h\nu \rightarrow CO + H \tag{71}$$
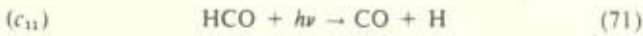
but reacts also with molecular and atomic oxygen

$$(c_{12a}) \qquad HCO + O_2 \rightarrow CO + HO_2 + 40 \text{ kcal} \tag{72a}$$

with a relatively high rate coefficient [*Washida et al.*, 1974]

$$c_{12a} = 5.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \tag{72b}$$

and is aeronomically more important ($O_2 \gg O$) than

$$(c_{12b_1}) \qquad HCO + O \rightarrow CO + OH + 87 \text{ kcal} \tag{72c}$$

$$(c_{12b_2}) \qquad HCO + O \rightarrow CO_2 + CH + 112 \text{ kcal} \tag{72d}$$

even with a high rate coefficient [*Washida et al.*, 1974]

$$c_{12b} = 2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \tag{72e}$$

The ratio c_{12b_1}/c_{12b_2} would be 1.4 according to *Westenberg and de Haas* [1972b] and about 1 according to *Mack and Thrush* [1973].

The reaction of HCO with OH is also rapid [*Morris and Niki*, 1971]

$$(c_{13}) \qquad HCO + OH \rightarrow H_2O + CO + 95 \text{ kcal} \tag{73a}$$

with

$$c_{13} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \tag{73b}$$

but is aeronomically less important than (c_{12}).

In addition to the reaction with NO of the methylperoxy radical CH_3O_2, other reactions must be introduced [*Levy*, 1972, 1973]:

$$(c_{14}) \qquad CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \tag{74a}$$

with [*Parkes et al.*, 1973]

$$c_{14} = 3.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \tag{74b}$$

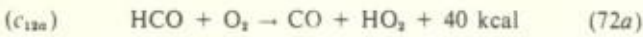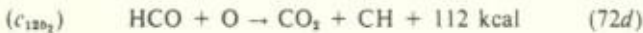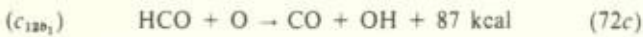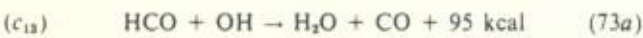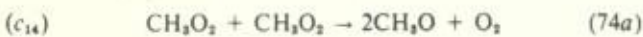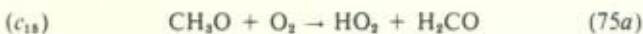which would be comparable with c_5 for concentrations of NO and CH_3O_2 of the same order of magnitude, but may be neglected in a first analysis; nevertheless, the removal of CH_3O can be considered by the reaction with O_2

$$(c_{15}) \qquad CH_3O + O_2 \rightarrow HO_2 + H_2CO \tag{75a}$$

with a slow rate coefficient (J. Heicklen, private communication, 1975) of the order of

$$c_{15} = 1.6 \times 10^{-13} e^{-3300/T} \tag{75b}$$

to lead to a lifetime of CH_3O of the order of a few hundreds to 1000 s in the lower stratosphere. However, it is necessary to consider the possible effect of HO_2 on CH_3O_2 as follows:

$$(c_{16}) \qquad CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \tag{76}$$
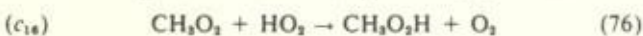
for which no measured rate coefficient is available. With a relatively high value there would be a competition between c_5 and c_{16} in which NO and HO_2 would be involved, respectively.

According to *Levy* [1972], CH_3O_2H either reacts with OH

$$(c_{17}) \qquad CH_3O_2H + OH \rightarrow H_2O_2 + CH_3O_2 \tag{77}$$
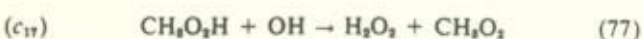
or is subject to photodissociation

$$(c_{18}) \qquad CH_3O_2H + h\nu \rightarrow CH_3O + OH \tag{78}$$
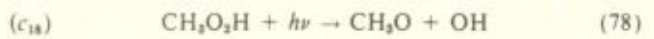
Finally, if methylperoxynitrite and methylperoxynitrate are formed, the photodissociation should be considered to be

$$(c_{19}) \qquad CH_3O_2NO + h\nu \rightarrow CH_3O_2 + NO \tag{79}$$

and

$$(c_{20}) \qquad CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2 \tag{80}$$
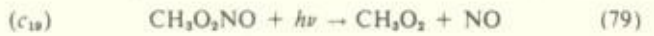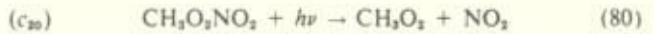
Reactions of CH_3, CH_3O, and CH_3O_2 with ozone have also been considered [*Simonaitis and Heicklen*, 1975a]. The experimental results are

$$(c_{21}) \qquad CH_3 + O_3 \rightarrow O_2 + H_2CO + H \tag{81a}$$
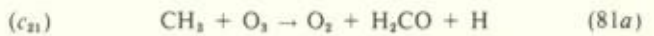
with

$$c_{21} = 5.4 \times 10^{-12} e^{-220/T} \tag{81b}$$

and lead to a value of the order of 5×10^{-13} cm^3 s^{-1} in the stratosphere, which is not sufficient to compete with reactions involving O_2. The reactions of CH_3O and CH_3O_2 with O_3 lead to $<2 \times 10^{-18}$ and $<2.4 \times 10^{-17}$ cm^3 s^{-1}, respectively, and are negligible.

If it is certain that the final result of the destruction of methane is the production of water vapor molecules and of carbon monoxide [*McConnell et al.*, 1971; *Wofsy et al.*, 1972], it is not yet clear how to determine the intermediate paths and their effect on ozone equilibrium [*Nicolet*, 1974; *Crutzen*, 1974a; *McConnell*, 1974]. Figure 7 shows how CH_3O_2, CH_3O, and H_2CO are three stratospheric constituents on the transformation routes of CH_4 into H_2O and CO. Unfortunately, it is not yet possible to deduce how the alkyperoxyl radical CH_3O_2 reacts simultaneously with NO_2, NO, and HO_2, the result being that the nitrogen dioxide production is fixed in comparison with the formaldehyde production leading to HO_2 and also to H_2. Ozone will be affected according to the various types of conversion of NO to NO_2 and CH_2 to OH and HO_2. It is critical that these various uncertainties be resolved by new and definite experimental measurements.

Thus with equations (61) to (81), it is possible to apply equilibrium conditions to H_2CO and HCO. Without neglecting any reaction:

$$n(H_2CO)[J_{H-HCO} + J_{H_2-CO} + c_7 n(OH) + c_9 n(O) + c_{10} n(H)]$$
$$= n(CH_4)[c_1 n(O) + c_{1a} {}^* n(O^*) + c_2 n(OH)] = n(HCO)$$
$$[J_{H-CO} + c_{12} n(O_2) + c_{13} n(OH)] + n(H_2CO) J_{H_2-CO} \tag{82}$$
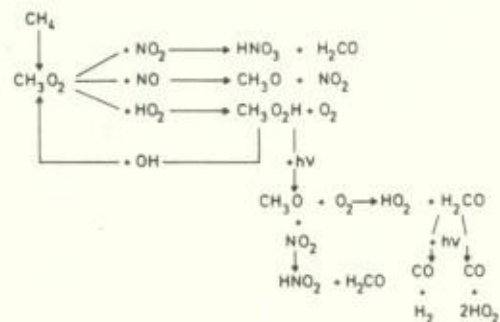
Fig. 7. Reaction scheme of the dissociation of methane in the stratosphere leading to the production of carbon monoxide. Direct reaction $CH_3 + O_2 \rightarrow H_2CO + OH$ should be added.

and with the principal reactions:

$$n(H_2CO)[J_{H-HCO} + J_{H_2-CO} + c_8n(OH)] = n(CH_4)[c_{1a}*n(O)$$

$$+ c_2n(OH)] = n(HCO)c_{12}n(O_2) + n(H_2CO)J_{H_2-CO} \quad (83)$$

This last equation shows that it is possible to deduce all aeronomic parameters if the photodissociation paths are sufficiently well-known and if the vertical distribution of stratospheric methane is determined.

If we consider the various reactions involving the production and loss mechanisms of H, OH, and HO_2 in CH_4 stratospheric aeronomy, we may write

$$\frac{dn(H)}{dt} + \frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt}$$

$$+ n(OH)[c_2n(CH_4) + 2c_{13}n(HCO) + 2c_{17}n(CH_3O_2H)]$$

$$= n(CH_4)[c_1n(O) + c_{1a}*n(O^*)]$$

$$+ 2n(H_2CO)J_{H-HCO} + n(CH_3O)c_{15}n(O_2) \quad (84)$$

With conditions (83), (84) becomes

$$\frac{dn(H)}{dt} + \frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + n(OH)c_2n(CH_4)[1 - X]$$

$$+ 2n(OH)[c_{13}n(HCO) + c_{17}n(CH_3O_2H)]$$

$$= n(CH_4)[c_1n(O) + c_{1a}*n(O^*)][1 + X]$$

$$+ n(CH_3O)c_{15}n(O_2) \quad (85)$$

with

$$X = \frac{2 J_{H-HCO}}{J_{H-HCO} + J_{H_2-CO} + c_8n(OH)} \quad (86)$$

If laboratory measurements [Sperling and Toby, 1973; T. Osif and J. Heicklen, private communication, 1975], which seem to indicate that $J_{H-HCO} > J_{H_2-CO} + c_8n(OH)$, in disagreement with other studies [McQuigg and Calvert, 1969; Calvert et al., 1972], are accepted, the ratio X could be greater than unity, and the steady state conditions of (85) would lead to

$$2n(OH)[c_{13}n(HCO) + c_{17}n(CH_3O_2H)]$$

$$= n(CH_4)\{[c_1n(O) + c_{1a}*n(O^*)][X + 1]$$

$$+ c_2n(OH)[X + 1]\} \quad (87)$$

which are the principal terms that must be introduced into the water vapor production when methane is present. Instead of (39), the additional terms (87) and the effect of H_2 lead to

$$n(OH)[a_{16}n(OH) + a_{17}n(HO_2) + a_{30}n(H_2O_2)$$

$$+ 2c_{13}n(HCO) + 2c_{17}n(CH_3O_2H)]$$

$$= \left[n(H_2O)a_{12}* + n(H_2)a_{24}* \right.$$

$$\left. + c_{1a}*n(CH_4)\frac{1 + X}{2} \right]n(O^*)$$

$$+ c_2\left(\frac{X - 1}{2}\right)n(CH_4)n(OH) \quad (88)$$

Two reactions, $(c_{1b}*)$ (equation (61d)) and (c_{7b}) (equation (67b)), are paths for the formation of H_2 that can be introduced in the stratosphere, and then (46) becomes

$$\frac{\partial n(H_2)}{\partial t} + \frac{\partial[n(H_2)w]}{\partial z} + n(H_2)[a_{24}*n(O^*) + a_{14}n(OH)]$$

$$= c_{1b}*n(O^*)n(CH_4) + n(H_2CO)c_{7b} + a_{23}n(H)n(HO_2) \quad (89)$$

A simple approximation of (88) is obtained when the production of H_2 is neglected and is written as follows:

$$a_{17}n(OH)n(HO_2) = a*n(O^*)[n(H_2O) + n(H_2) + \tfrac{3}{2}n(CH_4)]$$

$$+ \tfrac{1}{2}c_2n(OH)n(CH_4) \quad (90)$$

This equation represents the principal production processes of OH and HO_2 radicals that lead to the formation of stratospheric H_2O in a hydrogen-oxygen atmosphere involving methane. Nevertheless, it must be pointed out that the complex interactions among the various reactions require a more reliable data base in order to determine accurately their final action on the stratospheric ozone, particularly in the lower stratosphere.

REACTIONS IN A NITROGEN-HYDROGEN-OXYGEN ATMOSPHERE

The presence of nitrogen oxides in the upper atmosphere requires the production of atomic nitrogen [Nicolet, 1945, 1965a, b; Bates, 1952] or the dissociation of nitrous oxide [Bates and Witherspoon, 1952; Bates and Hays, 1967]. This problem was developed by Nicolet [1955a, b] in relation to the airglow. In the ionospheric regions, ionic reactions lead to excited atoms N(^2D) [Norton and Barth, 1970; Strobel et al., 1970; Nicolet, 1970b; Strobel, 1971a, b], which react rapidly with O_2 to form nitric oxide molecules. In the stratosphere, the reaction of the electronically excited oxygen atom O(^1D) with N_2O [Nicolet, 1971] has been considered as an important source of nitric oxide [Nicolet and Vergison, 1971; Crutzen, 1971; McElroy and McConnell, 1971; Nicolet and Peetermans, 1972; Johnston, 1972]. Cosmic rays [Warneck, 1972; Nicolet and Peetermans, 1972; Brasseur and Nicolet, 1973; Nicolet, 1975], must also be considered as an additional source, particularly at mean and high latitudes (geomagnetic latitude $\Phi > 45°$). In addition, a suggestion has been recently made by Crutzen et al. [1975] that the solar proton events are also stratospheric sources of nitric oxide. Another source of nitric oxide [McConnell, 1973; McConnell and McElroy, 1973] would be tropospheric ammonia, if it should reach the stratosphere. Finally, it might be useful to consider [Ackerman, 1975] the possible intrusion of nitrogen oxides into the stratosphere when they have a high mixing ratio at the tropopause level. Nevertheless, the possible action of past nuclear explosions [Foley and Ruderman, 1973] (and of a nuclear war [Hampson, 1974]) on the stratospheric nitric oxide production cannot be ignored. A definitive statement cannot be given if reference is made to the various publications indicating no detectable effect [Goldsmith et al., 1973; Bauer and Gilmore, 1975] or leading to a discernible effect [Johnston et al., 1973] on atmospheric ozone. Various types of analysis of ozone data should be made in order to understand the geographical distribution of the ozone fluctuations. An example is given in the analysis made by Ruderman and Chamberlain [1975]; they study the modulation of the production of nitric oxide by cosmic rays on stratospheric ozone and the possible effects related to artificial sources. However, correlations between solar activity and ozone may have various aspects [London and Oltmans, 1973; Paetzold, 1973] which indicate that statistical analyses must be combined with a knowledge of physical processes.

The formation of nitric oxide can be due to a three-body process

(b_1) $\qquad$ $N + O + M \rightarrow NO + M + 150$ kcal $\qquad$ (91a)
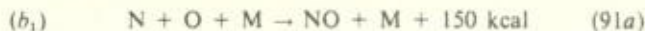
with a rate coefficient

$$b_1 = 9.1 \times 10^{-33}(300/T)^{1/2}n(M) \text{ cm}^3 \text{ s}^{-1} \qquad (91b)$$

deduced from measurements made by *Campbell and Gray* [1973]. However, before considering other nitric oxide formation processes, it is convenient to simplify the study of nitric oxide by analyzing its reactions with atomic oxygen and ozone, the principal active constituents of the chemosphere. First, there is the three-body process

(b_{2M}) $\qquad$ $O + NO + M \rightarrow NO_2 + M + 72$ kcal $\qquad$ (92a)

with a relatively high rate coefficient recommended by *Baulch et al.* [1973]

$$b_{2M} = 3.0 \times 10^{-33}e^{940/T}n(M) \text{ cm}^3 \text{ s}^{-1} \qquad (92b)$$

and a limited value at high pressure [*Gaedtke and Troe*, 1975]

$$b_{2M\infty} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (92c)$$
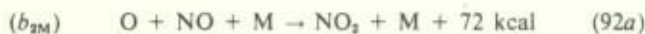
This three-body process leading to the formation of nitrogen dioxide must be compared with the radiative process

(b_2) $\qquad$ $O + NO \rightarrow NO_2 + h\nu$ $\qquad$ (92d)

which leads, according to *Becker et al.* [1972], at low pressure to the following value of the rate coefficient

$$b_2 = 4.2 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1} \qquad (92e)$$

and which becomes, according to the results of *Golde et al.* [1973],

$$b_{2\infty} = 1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \qquad (92f)$$

Two bimolecular processes must be considered as essential aeronomic reactions. One is the reaction with oxygen atoms

(b_3) $\qquad$ $O + NO_2 \rightarrow NO + O_2 + 46$ kcal $\qquad$ (93a)
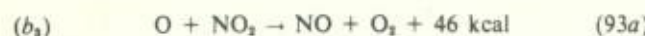
which is a relatively rapid reaction almost independent of temperature [*Davis et al.*, 1973b; *Slanger et al.*, 1973; *Bemand et al.*, 1974]. The following rate coefficient (average value) may be adopted

$$b_3 = 9.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \qquad (93b)$$

The other reaction of nitric oxide with ozone

(b_4) $\qquad$ $O_3 + NO \rightarrow NO_2 + O_2 + 48$ kcal $\qquad$ (94a)
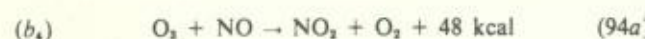
has an activation energy leading to $b_4 = 1.8 \times 10^{-14}$ cm³ s⁻¹ at 298 K, according to various laboratory measurements [*Johnston and Crosby*, 1954; *Clyne et al.*, 1964], and to

$$b_4 = 1.2 \times 10^{-12}e^{-1250/T} \text{ cm}^3 \text{ s}^{-1} \qquad (94b)$$

In addition to these reactions involving NO_2, the following photodissociation process occurs in a sunlit atmosphere

(b_5) $\qquad$ $NO_2 + h\nu(\lambda < 398 \text{ nm}) \rightarrow NO + O$ $\qquad$ (95)

Since the lifetime in the solar radiation field of NO_2 molecules is $200 < \tau_{NO_2} < 100$ s, a photoequilibrium [*Nicolet*, 1955a] must therefore exist and will lead to the ratio $n(NO_2)/n(NO)$:

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2n(O) + b_4n(O_3)}{J_{NO_2} + b_3n(O)} \qquad (96)$$

which is used in the stratosphere by all authors in the following form:

$$\frac{n(NO_2)}{n(NO)} = \frac{b_4n(O_3)}{J_{NO_2}} \qquad (97)$$

The scheme of the principal reactions related to the photochemistry of O-O₃ in the stratosphere is given in Figure 8 which corresponds to the following equation (see equations (20), (24), (26), and (96)):

$$\frac{dn(O_3)}{dt} + n(O_3)[a_6n(OH) + a_{6c}n(HO_2)]$$

$$+ n(O)[2k_3n(O_3) + a_5n(OH) + a_7n(HO_2) + 2b_3n(NO_2)]$$

$$= 2n(O_2)J_2 \qquad (98)$$

which shows that the correction term for the photoequilibrium region in the equation

$$n^2(O_3) = \frac{k_2}{k_3}n(M)n^2(O_2) \cdot \frac{J_2}{J_3(1 + A)} \qquad (99)$$

is

$$A = \frac{a_5n(OH) + a_7n(HO_2) + 2b_3n(NO_2)}{2k_3n(O_3)} \qquad (100)$$

Thus it can be concluded that nitrogen oxides play an important role in the vertical distribution of stratospheric ozone, and all authors have introduced their effects using reactions (b_3), (b_4), and (b_5), since the first work by *Crutzen* [1970]. This catalytic destruction

(b_3) $\qquad\qquad$ $NO_2 + O \rightarrow NO + O_2$

(b_4) $\qquad\qquad$ $NO + O_3 \rightarrow NO_2 + O_2$

(J_{NO_2}) $\qquad\qquad$ $NO_2 + h\nu \rightarrow NO + O$
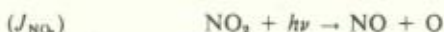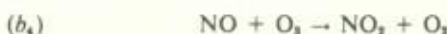
must have its major action above the ozone peak, where any departure from photoequilibrium conditions is not very great.

To determine the behavior of nitric oxide, it is necessary to examine aeronomic reactions in which atomic nitrogen is effectively involved. The only direct destruction of nitric oxide is its reaction with atomic nitrogen:

(b_6) $\qquad$ $N + NO \rightarrow N_2(v > 0) + O + 75$ kcal $\qquad$ (101a)
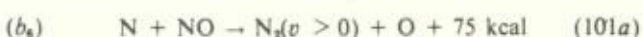
with a relatively high rate coefficient at 300 K [*Phillips and Schiff*, 1962]

$$b_6 = 2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (101b)$$

Between 298 and 670 K the rate coefficient is given by the ex-
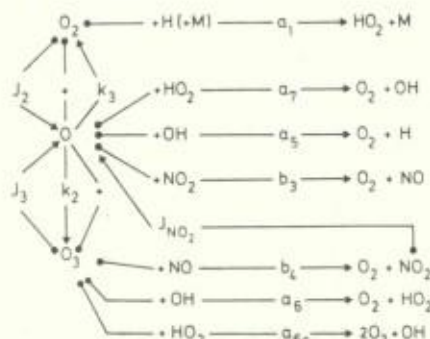
Fig. 8. Reactions occurring in a nitrogen-hydrogen-oxygen atmosphere that are related to the production and loss of odd oxygen.

pression

$$b_6 = (8.2 \pm 1.4) \times 10^{-11} e^{-|460 \pm 60|/T} \text{ cm}^3 \text{ s}^{-1} \quad (101c)$$

according to *Clyne and McDermid* [1975]. Such a reaction is not important in the stratosphere, except in the case of exceptional artificial disturbances when atomic nitrogen is produced.

The reaction of atomic nitrogen with molecular oxygen is a normal process to produce nitric oxide. A normal atom $N(^4S)$ leads to

$$(b_7) \qquad N(^4S) + O_2 \to NO(v > 0) + O + 32 \text{ kcal} \quad (102a)$$
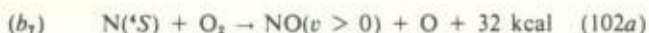
which has a high activation energy. The last laboratory measurement [*Becker et al.*, 1969] results in

$$b_7 = 5.5 \times 10^{-12} e^{-3200/T} \text{ cm}^3 \text{ s}^{-1} \quad (102b)$$

However, the reaction of molecular oxygen with excited atoms $N(^2D)$ is more rapid, since

$$(b_7^*) \qquad N(^2D) + O_2 \to NO + O + 87 \text{ kcal} \quad (102c)$$
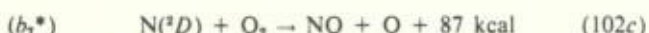
leads to an average value of the order of

$$b_7^* = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \quad (102d)$$

according to measurements made by *Lin and Kaufman* [1971], *Slanger et al.* [1971], and *Husain et al.* [1972].

In addition to the loss process of nitric oxide (b_6), which occurs only when atomic nitrogen is sufficiently abundant, it is necessary to consider the photodissociation process which occurs in the mesosphere but which can also play a role in the upper stratosphere [*Cieslik and Nicolet*, 1973]:

$$(b_8) \qquad NO + h\nu(\lambda < 1910 \text{ nm}) \to NO + O \quad (103)$$
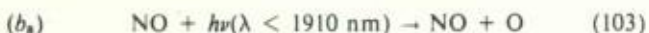
Thus the photoequilibrium conditions between N and NO can be defined by reactions (b_6), (b_7), and (b_8):

$$n(O_2)[b_7 n(N) + b_7^* n(N^*)] = n(NO)[J_{NO} + b_6 n(N)] \quad (104)$$

Other nitrogen oxides, such as nitrogen trioxide, tetroxide, and pentoxide, must be considered [*Nicolet*, 1965a]. In the ozonosphere, the reaction

$$(b_9) \qquad O_3 + NO_2 \to NO_3 + O_2 + 26 \text{ kcal} \quad (105a)$$
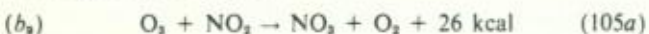
which leads to the production of nitrogen trioxide, must be introduced. Various recent laboratory measurements [*Johnston and Graham*, 1974b; *Huie and Herron*, 1974; *Davis et al.*, 1974a] give $(6.1 \pm 0.1) \times 10^{-18}$ at 200 K, corresponding to the average value

$$b_9 = 1.3 \times 10^{-13} e^{-2450/T} \text{ cm}^3 \text{ s}^{-1} \quad (105b)$$

Also, the three-body reaction

$$(b_{10}) \qquad O + NO_2 + M \to NO_3 + M + 50 \text{ kcal} \quad (106a)$$
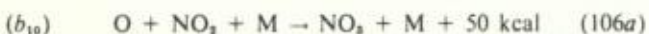
may occur in the region where atomic oxygen is present. Its rate coefficient [*Gaedtke and Troe*, 1975; *Hippler et al.*, 1975] is

$$b_{10M} = 8.0 \times 10^{-32} n(N_2) \text{ cm}^3 \text{ s}^{-1} \quad (106b)$$

and

$$b_{10M\infty} = 2.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \quad (106c)$$

For daytime conditions, such reactions are followed by the rapid process

$$(b_{11}) \qquad NO_3 + NO \to 2NO_2 + 22 \text{ kcal} \quad (107a)$$
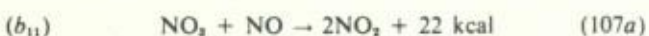
for which [*Harker and Johnston*, 1973; *Glänzer and Troe*, 1973] the following rate coefficient can be adopted ($T = 297$ K):

$$b_{11} = 8.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \quad (107b)$$

In addition, there are two possible photodissociation processes:

$$(J_{NO_3-O}) \qquad NO_3 + h\nu \to NO_2 + O \quad (108)$$

and

$$(J_{NO-O_2}) \qquad NO_3 + h\nu \to NO + O_2 \quad (109)$$
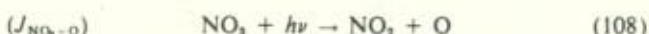
The photodissociation of $NO_3 \to NO + O_2$ was adopted for several years by various authors [*Crutzen*, 1973, 1974a; *Levy*, 1973] following *Johnston* [1974]. However, a recent communication by H. S. Johnston (unpublished manuscript, 1975) indicates that the photodissociation should be $NO_3 \to NO_2 + O$ and not process (109). Such a result is important, since it indicates that the nighttime process (b_9) of formation of nitrogen trioxide is counterbalanced by its daytime photodissociation. The destruction process of ozone in the lower stratosphere, which was considered as follows,

$$(b_9) \qquad NO_2 + O_3 \to NO_3 + O_2 \quad (110a)$$

$$(J_{NO-O_2}) \qquad NO_3 + h\nu \to NO + O_2 \quad (111)$$

must be replaced by

$$(J_{NO_2-O}) \qquad NO_3 + h\nu \to NO_2 + O \quad (110b)$$
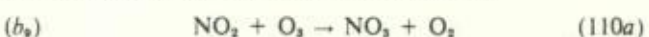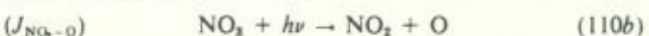
where (110a) and (110b) are associated. Nevertheless, there are other reactions involving NO_3, particularly for nighttime conditions in the lower stratosphere. The following processes should be considered

$$(b_{12}) \qquad NO_3 + NO_2 + M \to N_2O_5 + M + 22 \text{ kcal} \quad (112a)$$
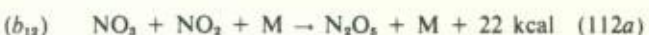
with the rate coefficients [see *Baulch et al.*, 1973]

$$b_{12M} = 2.8 \times 10^{-30} n(M) \text{ cm}^3 \text{ s}^{-1} \quad (112b)$$

and

$$b_{12M\infty} = 3.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \quad (112c)$$

which are reached at about 20 km. The endothermic reaction

$$(b_{13}) \qquad NO_3 + NO_2 \to O_2 + NO - 4 \text{ kcal} \quad (113a)$$
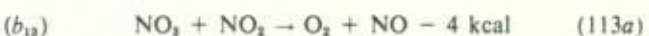
would have a rate coefficient [*Baulch et al.*, 1973]

$$b_{13} = 2.3 \times 10^{-13} e^{-1600/T} \text{ cm}^3 \text{ s}^{-1} \quad (113b)$$

leading to a value of about $1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ in the lower stratosphere. The reaction between two nitrogen trioxide molecules

$$(b_{14}) \qquad NO_3 + NO_3 \to 2NO_2 + O_2 + 18 \text{ kcal} \quad (114a)$$
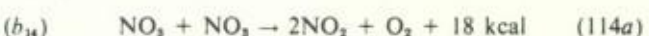
requires a high activation energy for stratospheric values. A suggested value for the rate coefficient [*Baulch et al.*, 1973] is

$$b_{14} = 5 \times 10^{-12} e^{-3000/T} \text{ cm}^3 \text{ s}^{-1} \quad (114b)$$

leading to a value of about $1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ in the lower stratosphere.

From this analysis of the various reactions of nitrogen trioxide, it is not clear if NO_3 can play a major role in stratospheric aeronomy. Its nighttime formation (reaction (b_9)) is always compensated for by daytime destruction processes. However, the action of nitroxyl, nitrous acid, and nitric acid must be considered before determining the exact stratospheric conditions. Nevertheless, the problem of nitrogen trioxide and pentoxide cannot be neglected during long nights when the action of their destruction processes is not important. In the

same way, the three-body association leading to nitrogen tetroxide should be considered only for sufficiently long night-time conditions

(b_{15}) $NO_2 + NO_2 + M \rightarrow N_2O_4 + M + 14$ kcal $(115a)$
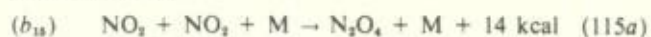
for which the rate coefficient is small [Clyne and Thrush, 1962]

$$b_{15} = 8 \times 10^{-34} n(M) \text{ cm}^3 \text{ s}^{-1}   (115b)$$

We will not analyze any reactions dealing with the formation and destruction of nitroxyl, since they cannot affect the essential stratospheric processes:

(b_{16a}) $H + NO + M \rightarrow HNO + M + 49$ kcal $(116a)$

(b_{16r}) $H + NO \rightarrow HNO + h\nu$ $(116b)$

(b_{17}) $H + HNO \rightarrow NO + H_2 + 55$ kcal (117)

(b_{18}) $OH + HNO \rightarrow NO + H_2O + 69$ kcal (118)

(b_{19}) $HO_2 + HNO \rightarrow NO + H_2O_2 + 40$ kcal (119)
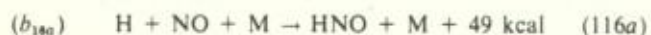
We consider now [Nicolet, 1965a] the various possible reactions leading to nitrous and nitric acids. We begin with the three-body association

(b_{20M}) $H + NO_2 + M \rightarrow HNO_2 + M + 80$ kcal $(120a)$

which is negligible in comparison with

(b_{20}) $H + NO_2 \rightarrow OH + NO + 29$ kcal $(120b)$
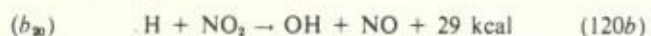
where (M. A. A. Clyne and P. B. Monkhouse, private communication, 1975)

$$b_{20} = 4.9 \times 10^{-10} e^{-410/T} \text{ cm}^3 \text{ s}^{-1}   (120c)$$

Reaction (b_{20}) is rapid, but it is less important than a three-body association with OH:

(b_{21}) $OH + NO + M \rightarrow HNO_2 + M + 60$ kcal $(121a)$
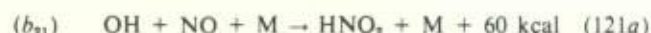
Measurements by Morley and Smith [1972] and Anderson et al. [1974] lead to the same result,

$$b_{21M} = 3.25 \times 10^{-32} e^{850/T} n(M) \text{ cm}^3 \text{ s}^{-1}   (121b)$$

with the possible limit [Sie et al., 1975b]

$$b_{21M\infty} = 1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}   (121c)$$

when the value $a_{58M\infty}$ (equation (56c)) is used for comparison. The reaction of OH with NO_2, which leads to nitric acid, is also extremely important:

(b_{22}) $OH + NO_2 + M \rightarrow HNO_3 + M + 53$ kcal $(122a)$
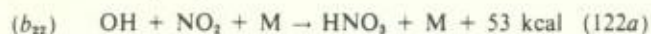
where [Anderson et al., 1974]

$$b_{22M} = 1.1 \times 10^{-31} e^{900/T} n(M) \text{ cm}^3 \text{ s}^{-1}   (122b)$$

and

$$b_{22M\infty} = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}   (122c)$$

A theoretical analysis of the rate coefficients b_{21} and b_{22} has been made by Tsang [1973] in order to determine the transition from b_M to $b_{M\infty}$ in the stratosphere.

However, a very recent experimental analysis by Anastasi et al. [1975] leads to the effective second-order rate coefficient for b_{22} with $n(N_2)$ varying from 1.6×10^{19} cm^{-3} to 3.2×10^{17} cm^{-3} between 220 and 358 K. Using such laboratory data it is possible to deduce directly the effective rate coefficients corresponding to the formation of nitric acid in the troposphere and stratosphere. The average values in Table 1 are obtained

for the standard U.S. atmospheres at latitudes $\varphi = 15°$ and $\varphi = 45°$, respectively (with an efficiency $n(N_2)/n(O_2) = \frac{1}{4}$).

The reaction involving HO_2 has not yet been observed.

(b_{23}) $HO_2 + NO + M \rightarrow HNO_3 + M + 63$ kcal (123)
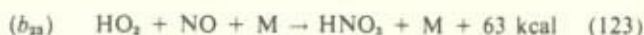
and may be neglected.

Before introducing the effect of the photolysis of HNO_2 and HNO_3, the action of H, OH, and HO_2 may be considered:

(b_{24}) $H + HNO_2 \rightarrow H_2 + NO_2 + 23$ kcal (124)
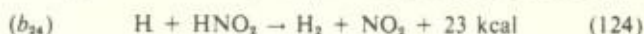
is not important compared with

(b_{25}) $OH + HNO_2 \rightarrow H_2O + NO_2 + 38$ kcal $(125a)$
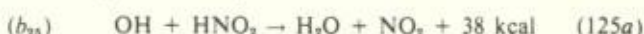
where

$$b_{25} = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}   (125b)$$

according to Cox [1974b]. The reaction of H with HNO_3

(b_{26}) $H + HNO_3 \rightarrow H_2O + NO_2 + 66$ kcal (126)

is negligible; $b_{26} < 2 \times 10^{-15}$ cm^3 s^{-1}, according to Chapman and Wayne [1974], as the reaction with atomic oxygen $b < 2 \times 10^{-17}$ cm^3 s^{-1}. But the action of OH is important

(b_{27}) $OH + HNO_3 \rightarrow H_2O + NO_3 + 15$ kcal $(127a)$
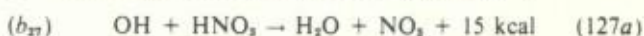
where

$$b_{27} = 0.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}   (127b)$$

according to the most recent measurement [Zellner and Smith, 1974; Smith and Zellner, 1975].

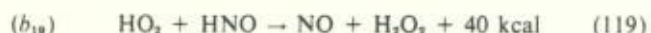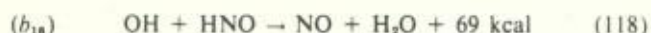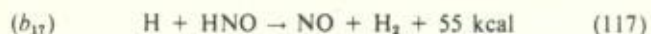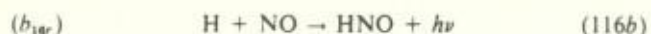Another reaction which should be introduced [Simonaitis and Heicklen, 1974a; Cox and Derwent, 1975] is

(b_{28a}) $HO_2 + NO_2 \rightarrow HNO_2 + O_2 + 34$ kcal $(128a)$

with a reported rate coefficient

$$b_{28a} = 1.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}   (128b)$$

However, more recent results [Simonaitis and Heicklen, 1975c] seem to suggest that an important reaction of HO_2 with NO_2 could be a process like the following:

(b_{28b}) $HO_2 + NO_2(+M) \rightarrow HO_2NO_2(+M)$ $(128c)$
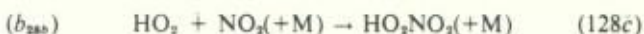
leading perhaps to a long-lived complex at stratospheric temperatures.

The important reaction

(b_{29}) $HO_2 + NO \rightarrow OH + NO_2$ $(129a)$
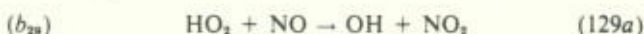
which was introduced in the determination of the ratio $n(OH)/n(HO_2)$ in the lower stratosphere, (equation (57)), has a rate coefficient which is still not known with precision. Davis et al. [1973c] and Payne et al. [1973] give

$$b_{29} = 3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}   (129b)$$

TABLE 1.   Average Values of b_{22} (cm s^{-1}) at Two Latitudes

Altitude, km	$\varphi = 45°$	$\varphi = 15°$
12	1.5×10^{-11}	1.2×10^{-11}
15	1.3×10^{-11}	1.6×10^{-11}
17	1.3×10^{-11}	1.8×10^{-11}
20	6.3×10^{-12}	1.2×10^{-11}
25	3.3×10^{-12}	3.3×10^{-12}
30	1.6×10^{-12}	1.4×10^{-12}
35	7.8×10^{-13}	6.7×10^{-12}

with a stated uncertainty of a factor of 3. *Hack et al.* [1975] give

$$b_{29} = 2 \times 10^{-11} e^{-1200/T} \text{ cm}^3 \text{ s}^{-1} \qquad (129c)$$

whereas *Simonaitis and Heicklen* [1975c] find $b_{29} = (1.02 \pm 0.2) \times 10^{-12}$ at 300 K based on $a_{27} = 3.3 \times 10^{-12}$ cm^3 s^{-1} and *Cox and Derwent* [1975] obtain $b_{29} = 1.2 \times 10^{-12}$ cm^3 s^{-1} at 296 K. The reactions of hydrogen peroxide with nitrogen dioxide and nitric oxide are too slow to play a role in the stratosphere. According to *Gray et al.* [1972]

(b_{30}) $\qquad$ NO + H$_2$O$_2 \rightarrow$ OH + HNO$_2$ + 11 kcal $\qquad$ (130a)
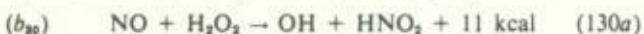
has a rate coefficient

$$a_{30} < 5 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1} \qquad (130b)$$

With the formation of dinitrogen pentoxide (reaction (b_{12})), it is necessary to introduce the reaction with H$_2$O which is often considered. According to *Morris and Niki* [1973],

(b_{31}) $\qquad$ N$_2$O$_5$ + H$_2$O $\rightarrow$ 2HNO$_3$ + 10 kcal $\qquad$ (131a)
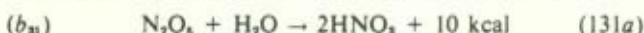
would have a rate coefficient at 250 K of

$$b_{31} < 3 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1} \qquad (131b)$$

However, the photodissociation must be considered

(b_{32a}) $\quad$ N$_2$O$_5$ + $h\nu(\lambda < 380$ nm$) \rightarrow$ NO$_2$ + NO$_3$ $\quad$ (132a)
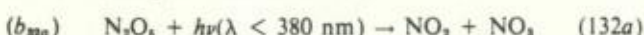
and the dissociation by collision

(b_{32b}) $\quad$ N$_2$O$_5$ + M $\rightarrow$ NO$_3$ + NO$_2$ + M $-$ 22 kcal $\quad$ (132b)
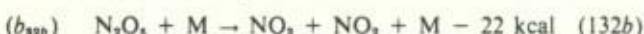
where [*Baulch et al.*, 1973; *Niki*, 1974]

$$b_{32b} = 2.2 \times 10^{-5} e^{-9700/T} \text{ cm}^3 \text{ s}^{-1} \qquad (132c)$$

or

$$b_{32b} = 0.104 \text{ s}^{-1} \qquad (132d)$$

at 1 atm and 297 K [*Harker and Johnston*, 1973].

Finally, particular attention must be given to the photodissociation of nitrous and nitric acids.

The primary products of HNO$_2$ photodissociation are

(J_{OH-NO}) $\quad$ HNO$_2$ + $h\nu(\lambda < 585$ nm$) \rightarrow$ OH + NO $\quad$ (133)

and

(J_{H-NO_2}) $\quad$ HNO$_2$ = $h\nu(\lambda < 366$ nm$) \rightarrow$ H + NO$_2$ $\quad$ (134)
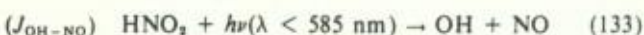
According to *Cox* [1974a], the second process may correspond to about 10% of the overall photodissociation.

The photodissociation of HNO$_3$ occurs according to the process [*Johnston and Graham*, 1973, 1974a]

(J_{OH-NO_2}) $\quad$ HNO$_3$ + $h\nu(\lambda < 320$ nm$) \rightarrow$ OH + NO$_2$ $\quad$ (135)
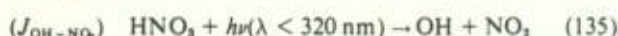
with a quantum yield equal to unity at all wavelengths.

After this detailed analysis of the various reactions involving nitrogen oxides, we will consider the principal chemical and photochemical equations. For daytime conditions, photochemical equilibrium can be considered immediately for N$_2$O$_5$, NO$_3$, HNO$_2$, and NO$_2$, since their photodissociations are sufficiently rapid. We may write for N$_2$O$_5$, NO$_3$, HNO$_2$, and NO$_2$, respectively,

$$n(\text{N}_2\text{O}_5)[b_{32} + b_{31}n(\text{H}_2\text{O})] = b_{12}n(\text{M})n(\text{NO}_2)n(\text{NO}_3) \qquad (136)$$

$n(\text{NO}_3)[J_{\text{NO}_2-\text{O}} + b_{11}n(\text{NO}) + b_{12}n(\text{M})n(\text{NO}_2)]$

$\qquad = n(\text{NO}_2)[b_9n(\text{O}_3) + b_{10}n(\text{M})n(\text{O})] + b_{27}n(\text{OH})n(\text{HNO}_3)$

$\qquad\qquad + b_{32}n(\text{N}_2\text{O}_5) \qquad (137)$

$n(\text{HNO}_2)[J_{\text{OH}-\text{NO}} + J_{\text{H}-\text{NO}_2} + b_{28}n(\text{OH})]$

$\qquad = b_{21}n(\text{M})n(\text{NO})n(\text{OH}) + b_{29}n(\text{NO}_2)n(\text{HO}_2) \qquad (138)$

$n(\text{NO}_2)[J_{\text{NO}_2} + b_3n(\text{O}) + b_9n(\text{O}_3) + b_{10}n(\text{M})n(\text{O})$

$\qquad + b_{12}n(\text{M})n(\text{NO}_3) + b_{22}n(\text{M})n(\text{OH}) + b_{29}n(\text{HO}_2)]$

$\qquad = n(\text{NO})[b_2n(\text{M})n(\text{O}) + b_4n(\text{O}_3) + 2b_{11}n(\text{NO}_3)$

$\qquad + b_{29}n(\text{HO}_2) + c_{6a}n(\text{CH}_3\text{O}_2)] + n(\text{HNO}_2)[J_{\text{H}-\text{NO}_2}$

$\qquad + b_{28}n(\text{OH})] + n(\text{HNO}_3)J_{\text{OH}-\text{NO}_2} + n(\text{NO}_3)J_{\text{NO}_2-\text{O}} \qquad (139)$

In addition, chemical equilibrium must exist for atomic nitrogen, and we may write

$n(\text{N})[b_1n(\text{M})n(\text{O}) + b_6n(\text{NO}) + b_7n(\text{O}_2)]$

$\qquad\qquad = n(\text{NO})J_{\text{NO}} + P(\text{N}) \qquad (140)$

where $P(\text{N})$ is the direct production of nitrogen atoms.

With the introduction of the reactions (c_1) to (c_{20}) involving the dissociation of methane, (b_1) to (b_{32}) involving all nitrogen oxides, and (a_1) to (a_{38}) involving all hydrogen reactions, the equations governing the rates of change of the concentration of and atomic oxygen become

$$\frac{dn(\text{O}_3)}{dt} + n(\text{O}_3)[J_3 + k_3n(\text{O})$$

$\qquad + a_2n(\text{H}) + a_6n(\text{OH}) + a_{6c}n(\text{HO}_2)$

$\qquad + b_4n(\text{NO}) + b_9n(\text{NO}_2)] = k_2n(\text{M})n(\text{O}_2)n(\text{O}) \qquad (141)$

$$\frac{dn(\text{O})}{dt} + n(\text{O})[2k_1n(\text{M})n(\text{O}) + k_2n(\text{M})n(\text{O}_2) + k_3n(\text{O}_3)$$

$\qquad + a_5n(\text{OH}) + a_7n(\text{HO}_2) + a_{31}n(\text{H}_2\text{O}_2) + b_1n(\text{M})n(\text{N})$

$\qquad + b_2n(\text{M})n(\text{NO}) + b_3n(\text{NO}_2) + b_{10}n(\text{M})n(\text{NO}_2)]$

$\qquad = 2n(\text{O}_2)J_2 + n(\text{O}_3)J_3 + n(\text{NO})J_{\text{NO}} + n(\text{NO}_2)J_{\text{NO}_2}$

$\qquad + n(\text{NO}_3)J_{\text{NO}_2-\text{O}} + n(\text{N})[b_6n(\text{NO} + b_7n(\text{O}_2)] \qquad (142)$

Since atomic oxygen (equation (142)) and atomic nitrogen (equation (140)) are always in photochemical equilibrium in the stratosphere, the ozone equation (141) becomes ($a_2n(\text{H})$ and $2k_1n(\text{O})$ being neglected)

$$\frac{dn(\text{O}_3)}{dt} + n(\text{O}_3)[2k_2n(\text{O}) + a_6n(\text{OH}) + a_{6c}n(\text{HO}_2)$$

$\qquad + b_4n(\text{NO}) + b_9n(\text{NO}_2)] + n(\text{O})\{a_5n(\text{OH})$

$\qquad + a_7n(\text{HO}_2) + a_{31}n(\text{H}_2\text{O}_2) + 2b_1n(\text{M})n(\text{N})$

$\qquad + b_2n(\text{M})n(\text{NO}) + [b_3 + b_{10}n(\text{M})]n(\text{NO}_2)\}$

$\qquad = 2n(\text{O}_2)J_2 + 2n(\text{NO})J_{\text{NO}} + P(\text{N})$

$\qquad + n(\text{NO}_2)J_{\text{NO}_2} + n(\text{NO}_3)J_{\text{NO}_2-\text{O}} \qquad (143)$

Thus the addition of nitrogen oxides NO and NO$_2$, which destroy odd oxygen by various reactions involving ozone and atomic oxygen, must be considered with its counterpart, the photodissociation of NO, NO$_2$, and NO$_3$ and the N formation, as production processes in addition to the photodissociation of molecular oxygen. This double effect of nitrogen oxides should be considered, particularly in polluted atmospheres or in the atmospheric regions where atomic oxygen production by photodissociation of molecular oxygen is small.

Having introduced in (143) the simultaneous effects of

(136), (137), and (138) representing the photoequilibrium equations of N_2O_5, NO_3, and NO_2, respectively, we may write (reactions (b_1), (b_2), and (b_{31}) being neglected)

$$\frac{dn(O_3)}{dt} + n(O_3)[2k_3n(O) + a_6n(OH) + a_{6c}n(HO_2)]$$

$$+ n(O)[a_5n(OH) + a_7n(HO_2)$$

$$+ a_{31}n(H_2O_2) + 2b_3n(NO_2)]$$

$$= -n(NO_2)[b_{22}n(M)n(OH) + b_{28}n(HO_2)]$$

$$- 2k_{31}n(H_2O)n(N_2O_5) + 2n(O_2)J_2$$

$$+ n(NO)[2J_{NO} + b_{29}n(HO_2) + c_{5a}n(CH_3O_2)]$$

$$+ P(N) + n(HNO_3)[J_{OH-NO_2} + b_{27}n(OH)]$$

$$+ n(HNO_2)[J_{H-NO_2} + b_{25}n(OH)] \qquad (144)$$

The fact that the equation governing the rate of change of the concentration of nitric acid is

$$\frac{dn(HNO_3)}{dt} + n(HNO_3)[J_{OH-NO_2} + b_{27}n(OH)]$$

$$= b_{22}n(M)n(OH) + n(NO_2) + 2b_{31}n(H_2O)n(N_2O_5) \quad (145)$$

indicates that photoequilibrium conditions are not reached rapidly, particularly in the lower stratosphere ((J_{OH-NO_2}) being too small), and it is difficult to determine the exact effect of HNO_3 in (144). Nevertheless, by introducing its photochemical equilibrium value in (144), the ozone equation related to stratospheric chemical conditions is simply written:

$$\frac{dn(O_3)}{dt} + n(O_3)[2k_3n(O) + a_6n(OH) + a_{6c}n(HO_2)]$$

$$+ n(O)[a_5n(OH) + a_7n(HO_2)$$

$$+ a_{31}n(H_2O_2) + 2b_3n(NO_2)]$$

$$= 2n(O_2)J_2 + n(NO)[2J_{NO} + c_{5a}n(CH_4O_2)]$$

$$+ P(N) + n(HNO_2)J_{H-NO_2}$$

$$+ n(OH)[b_{25}n(HNO_2) + b_{27}n(HNO_3)]$$

$$+ n(HO_2)[b_{29}n(NO) - b_{28}n(NO_2)]$$

$$= 2n(O_2)J_2 + n(NO)[2J_{NO} + b_{21}n(M)n(OH)$$

$$+ b_{29}n(HO_2) + c_{5a}n(CH_3O_2)] + P(N)$$

$$+ n(HNO_3)b_{27}n(OH) - n(HNO_2)J_{OH-NO} \quad (146)$$

Thus the action of nitrogen oxides leads to ozone destruction by the reaction of NO_2 with O. Since numerical values of the various parameters in the stratosphere and troposphere lead to

$$n(O) = \frac{n(O_3)J_3 + n(NO_2)J_{NO_2}}{k_2n(M)n(O_2)} \qquad (147)$$

the general chemical equation (146) for the ozone concentration in the stratosphere is

$$\frac{dn(O_3)}{dt} + \frac{2k_3J_3}{k_2n(M)n(O_2)} n^2(O_3)\left[1 + \frac{n(NO_2)J_{NO_2}}{n(O_3)J_3}\right]$$

$$+ n(O_3)\Big\{[a_6n(OH) + a_{6c}n(HO_2)]$$

$$+ \frac{J_3}{k_2n(M)n(O_2)}\left[1 + \frac{n(NO_2)J_{NO_2}}{n(O_3)J_3}\right][a_5n(OH)$$

$$+ a_7n(HO_2) + a_{31}n(H_2O_2) + 2b_3n(NO_2)]\Big\}$$

$$= 2n(O_2)J_2 + n(NO)[2J_{NO} + b_{21}n(M)n(OH)$$

$$+ b_{29}n(HO_2) + c_{5a}n(CH_3O_2)] + P(N)$$

$$+ n(HNO_3)b_{27}n(OH) - n(HNO_2)J_{OH-NO} \quad (148)$$

Such an equation can represent disturbed conditions in the stratosphere when the photodissociation rate of NO_2 is not negligible in comparison with the photodissociation rate of ozone. In the normal stratosphere, it may be assumed that

$$n(NO_2)J_{NO_2} < n(O_3)J_3 \qquad (149)$$

and the general equation (148) can be simplified as follows:

$$\frac{dn(O_3)}{dt} + \frac{2k_3J_3}{k_2n(M)n(O_2)} n^2(O_3)$$

$$+ n(O_3)\Big\{[a_6n(OH) + a_{6c}n(HO_2)]$$

$$+ \frac{J_3}{k_2n(M)n(O_2)} [a_5n(OH)$$

$$+ a_7n(HO_2) + a_{31}n(H_2O_2) + 2k_3n(NO)]\Big\}$$

$$= 2n(O_2)J_2 + n(NO)[2J_{NO} + b_{21}n(M)n(OH)$$

$$+ b_{29}n(HO_2) + c_5n(CH_3O_2)] + P(N)$$

$$+ n(HNO_3)b_{27}n(OH) - n(HNO_2)J_{OH-NO} \quad (150)$$

Since $J_3/k_2n(M)n(O_2)$ increases with height, the effective action (b_3) of NO_2 on the ozone concentration cannot reach its principal action in the lower stratosphere (below 20 km). In this region the effect of reactions a_6 and a_{6c} depends on the absolute value of the OH and HO_2 concentrations which is difficult to determine. It seems therefore that there is not yet an answer to the question of what the exact parts of transport and chemistry are in the ozone behavior below its concentration peak.

Another remark may be made here if we consider the production term in the general equation (146). There is, in addition to the normal production by molecular oxygen $2n(O_2)J_2$, other terms which are of the same order of magnitude in the lower stratosphere. Special attention is particularly required when there is an artificial injection of nitric oxide and water vapor into the stratosphere. In particular, the following term

$$n(HO_2)[b_{29}n(NO) - b_{28}n(NO_2)] \qquad (151)$$

must be introduced as an addition to the ozone production; but an exact knowledge of b_{28} and particularly of b_{29} is required.

Finally, the ratio $n(OH)/n(HO_2)$, which must be known in order to determine the concentration of the hydroxyl and hydroperoxyl radicals (see equations (88) and (90)), is given, with the effect of nitrogen oxides, by

$$n(HO_2)[a_{6c}n(O_3) + a_7n(O) + a_{17}n(OH) + 2a_{27}n(HO_2)$$

$$+ b_{29}n(NO) + b_{28}n(NO_2)] = n(OH)[a_5n(O) + a_6n(O_3)$$

$$+ a_{19}n(H_2) + a_{30}n(H_2O_2) + a_{34}n(CO)$$

$$+ c_4n(H_2CO) + c_2Xn(CH_4)] \qquad (152a)$$

and, after having introduced various numerical values, keeping only the principal terms for the stratosphere, by

$$n(HO_2)[a_6 n(O_3) + a_7 n(O) + b_{29} n(NO)]$$

$$= n(OH)[a_5 n(O) + a_4 n(O_3) + a_{30} n(CO)] \qquad (152b)$$

The additional effect of nitric acid leads to an additional term in equation (88) or (90) which gives the OH concentration, if the ratio $n(HO_2)/n(OH)$ is known. The equation, which must be applied to the stratosphere, may be written

$$n(OH)[n(HO_2)a_{17} + n(HNO_3)b_{27}]$$

$$= a^* n(O^*)\left[n(H_2O) + n(H_2) + \frac{1 + X}{2} n(CH_4) \right]$$

$$+ c_2\left(\frac{X - 1}{2} \right) n(CH_4) n(OH) \qquad (153)$$

where $X > 1$, according to (86).

Figure 9 [*Nicolet*, 1974] shows the importance of the reaction (a_{17}) (OH + HO$_2$ → H$_2$O + O$_2$) if the rate coefficient reaches 2×10^{-10} cm^3 s^{-1}. Nevertheless, the action of nitric acid must be introduced and should determine strong geographic variations associated with the variation of the tropopause, as can be seen from an analysis of the HNO$_3$ behavior in the lower stratosphere.

Furthermore, the differential equation for nitric oxide must be written as follows:

$$\frac{dn(NO)}{dt} + n(NO)[J_{NO} + b_2 n(M)n(O) + b_n n(N)$$

$$+ b_4 n(O_3) + b_{11} n(NO_3)$$

$$+ b_{21} n(M)n(OH) + b_{29} n(HO_2) + c_{5a} n(CH_3O_2)]$$

$$= b_1 n(M)n(O)n(N) + 2b_5 n(N)n(NO_2)$$

$$+ b_7 n(N)n(O_2^*) + n(NO_2) J_{NO_2} + b_3 n(O)n(NO_2)$$

$$+ n(HNO_2) J_{OH-NO} + P(NO) \qquad (154)$$

where $P(NO)$ is the direct production of nitric oxide molecules.
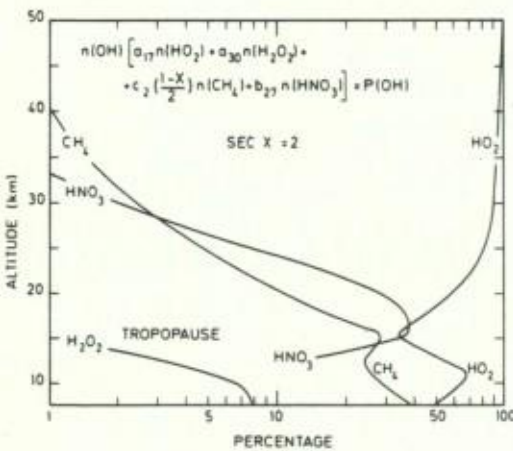
Fig. 9. Examples of possible profiles (percentages) of various terms determining the concentration of hydroxyl radical, using profiles of Figures 4 and 5. The effect of CH$_4$ corresponds to a certain value X which was obtained in 1973 for the photodissociation of formaldehyde H$_2$ + CO and H + COH, and its effect is very sensitive to the value of X used.

By combining all equilibrium equations involving N$_2$O$_5$ (136), NO$_3$ (137), HNO$_2$ (138), NO$_2$ (139), and N (137), with the differential equations (145) and (154) involving HNO$_3$ and NO, respectively, we can write the differential equation for odd nitrogen:

$$\frac{dn(NO)}{dt} + \frac{dn(HNO_3)}{dt}$$

$$= P(N) + P(NO) - 2b_6 n(N)n(NO) \qquad (155a)$$

or, introducing the equilibrium value (140) for the atomic nitrogen concentration,

$$\frac{dn(NO)}{dt} + \frac{dn(HNO_3)}{dt} + 2b_6 J_{NO} \frac{n^2(NO)}{b_6 n(NO) + b_7 n(O_2)}$$

$$= \frac{b_7 n(O_2) - b_6 n(NO)}{b_7 n(O_2) + b_6 n(NO)} P(N) + P(NO) \qquad (155b)$$

where

$$b_7 n(O_2) > b_6 n(NO) \qquad (155c)$$

Let us use the ratio

$$n(NO_y)/n(NO) = R \qquad (156a)$$

where

$$n(NO_y) = n(HNO_3) + n(NO) \qquad (156b)$$

in order to write (155b) as follows [*Brasseur and Nicolet*, 1973]:

$$\frac{\partial n(NO_y)}{\partial t} + 2b_6 J_{NO} \frac{n^2(NO_y)}{R[b_6 n(NO_y) + Rb_7 n(O_2)]}$$

$$+ \text{div } \Phi(NO_y) = \frac{Rb_7 n(O_2) - b_6 n(NO_y)}{Rb_7 n(O_2) + b_6 n(NO_y)} P(N) + P(NO) \qquad (157)$$

if the control by eddy diffusion transport is introduced.

Taking into account condition (155c) and considering that the production $P(N)$ is compensated for by the rapid transformation of N in NO under normal conditions, the following equation pertaining to the variation of NO$_y$ can be written as follows at the stratopause level, where NO$_y$ = NO and $J_{NO} \neq 0$:

$$\frac{\partial n(NO)}{\partial t} + \frac{2b_6 J_{NO}}{b_7 n(O_2)} n^2(NO) + \text{div } \Phi(NO) = P(NO) \quad (158a)$$

and in the lower stratosphere

$$\frac{\partial n(NO_y)}{\partial t} + \text{div } \Phi(NO_y) = P(NO) \qquad (158b)$$

since $J_{NO} = 0$; the photodissociation of nitric oxide plays an important role in the mesosphere, a reduced role in the upper stratosphere, and a negligible role in the lower stratosphere.

Thus the nitrogen oxide concentrations, and particularly those of HNO$_3$, NO, and NO$_2$, must depend on atmospheric conditions in the lower stratosphere (see Figure 10) [*Brasseur and Nicolet*, 1973], and their behavior will be related to the variation of the tropopause. The action of the advection and various dynamic processes at the tropopause level must modify the lower boundary conditions, which must be known in order to resolve (158b). As far as HNO$_3$ is concerned, it is soluble in water in the troposphere [*Stedman et al.*, 1975b], and
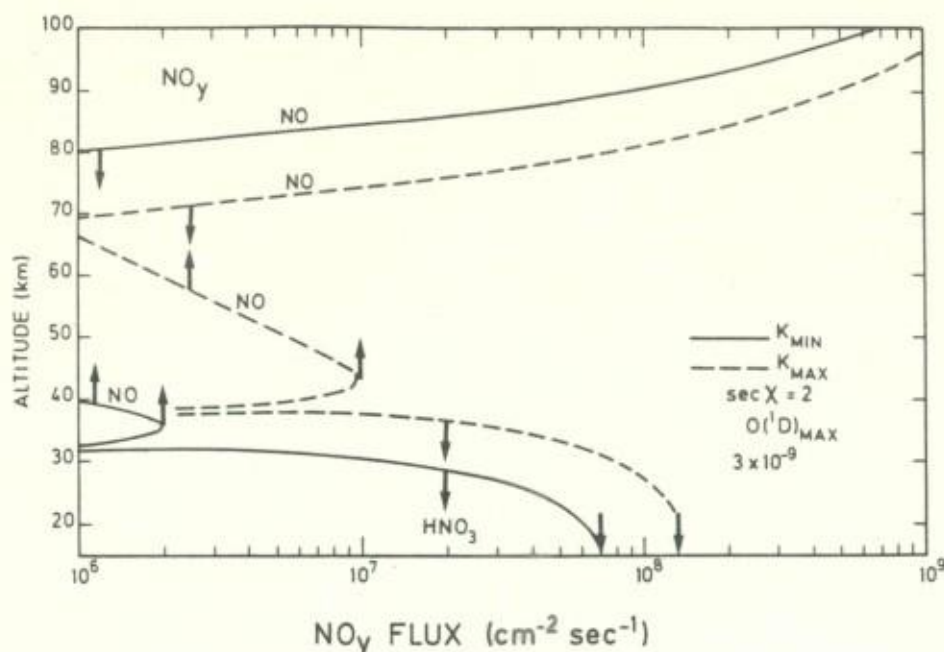
Fig. 10. Examples of vertical transport of NO and HNO_3 for arbitrary conditions of eddy diffusion coefficients K_{max} and K_{min} and upper and lower boundary conditions at 100 and 15 km; upward and downward currents are shown by NO at the stratopause and by HNO_3 at the tropopause, respectively.

its lower boundary conditions are defined by its tropospheric behavior.

It is clear that, at the present time, it is extremely difficult to have a correct view of the various processes involved in the determination of the vertical distribution of ozone in the lower stratosphere and also of the absolute value of its concentration. In particular, the ratio $n(OH)/n(HO_2)$ is related to $n(NO)$ and $n(CO)$ in the lower stratosphere, while $n(HNO_3)$ depends on $n(OH)$, and $n(OH)$ is not independent of $n(HNO_3)$.

REACTIONS IN A CHLORINE-NITROGEN-HYDROGEN-OXYGEN ATMOSPHERE

As was mentioned in the introduction, the role of chlorine compounds as catalysts for the destruction of odd oxygen in the stratosphere must be considered. Since the proposal made by *Stolarski and Cicerone* [1974] of a sink for stratospheric ozone by the oxides of chlorine, ClO_x, a first publication by *Molina and Rowland* [1974a] has shown the possible action of the chlorofluoromethanes, in particular of the trichlorofluoromethane, $CFCl_3$ [*Lovelock*, 1971, 1972, 1974; *Lovelock et al.*, 1973; *Wilkniss et al.*, 1973, 1975a], and of the dichlorofluoromethane, CF_2Cl_2 [*Su and Goldberg*, 1973], which are observed in the troposphere. The action of Freon production [*McCarthy*, 1974] on stratospheric ozone has been analyzed in different ways by several authors [*Rowland and Molina*, 1975; *Crutzen*, 1974b; *Cicerone et al.*, 1974, 1975b; *Wofsy et al.*, 1975]. Another publication by *Molina and Rowland* [1974b] on the stratospheric photodissociation of the carbon tetrachloride molecule, CCl_4, observed in the troposphere [*Lovelock et al.*, 1973, 1974; *Murray and Riley*, 1973; *Su and Goldberg*, 1973; *Wilkniss et al.*, 1973, 1975b; *Simmonds et al.*, 1974], shows that such a constituent, which is perhaps partly of natural origin, is photodissociated in the stratosphere and could play a certain role in the destruction of stratospheric ozone. Finally, the action of chloromethane, CH_3Cl, has been introduced very recently by *Cicerone et al.*

[1975a] and must be considered at the present time as the principal halocarbon of the atmosphere, since its natural concentration is relatively high [*Lovelock*, 1975; R. A. Rasmussen, private communication, 1975].

The problem of chlorine species in the stratosphere begins after their transport from the troposphere by their photodissociation in the ozonosphere. Among the various dissociation processes, we may consider the following:

(d_{1a}) $Cl_2 + h\nu(\lambda < 483 \text{ nm}) \rightarrow 2Cl$ (159a)

is photodissociated in the stratosphere and troposphere by radiation of $\lambda > 300$ nm [*Seery and Britton*, 1964] and cannot be an important minor constituent.

(d_{1b}) $HCl + h\nu(\lambda < 220 \text{ nm}) \rightarrow H + Cl$ (159b)
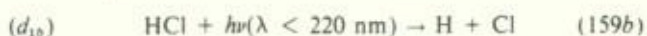
is photodissociated for wavelengths shorter than 300 nm. Laboratory measurements [*Romand*, 1949; *Myer and Samson*, 1970] which have been made between $\lambda = 207$ and 139 nm indicate that the dissociation of hydrogen chloride can only occur in the stratosphere.

(d_{1c}) $ClO + h\nu(\lambda < 263 \text{ nm}) \rightarrow Cl + O$ (159c)
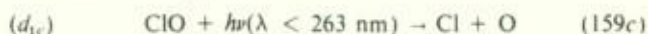
The continuous absorption occurs beyond 263 nm [*Durie and Ramsay*, 1958], but there is a predissociation at 290 nm in the $(7 - 0)$ band. The total photodissociation is therefore not easy to determine. With the cross sections as given by *Johnston et al.* [1969], it may be concluded that the ClO photodissociation is related to the stratospheric ozone concentration.

The absorption cross sections for photodissociation of Freon have been determined by *Rowland and Molina* [1975] after earlier measurements by *Doucet et al.* [1973]; the dominant photochemical process is

(d_{1d}) $CFCl_3 + h\nu(\lambda < 226 \text{ nm}) \rightarrow CFCl_2 + Cl$ (160a)
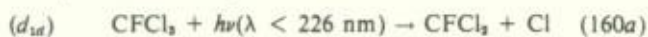
for which laboratory measurements [*Marsh and Heicklen*,

1965; *Jayanty et al.*, 1975*b*] indicate that the quantum yield is unity.

For CF$_2$Cl$_2$, very recent results by *Milstein and Rowland* [1975] and *Jayanty et al.* [1975*b*], after determination of the absorption cross sections [*Rowland and Molina*, 1975], indicate that

$$(d_{1e}) \qquad CF_2Cl_2 + h\nu(\lambda < 215 \text{ nm}) \rightarrow CF_2Cl + Cl \qquad (160b)$$
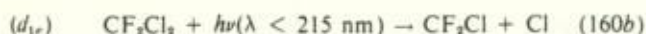
for which the quantum yield is unity for the photooxidation by 184.9- and 213.9-nm photolysis in the presence of O$_2$. Thus both CFCl$_3$ and CF$_2$Cl$_2$ absorb solar radiation in the stratosphere and cannot be photolyzed in the troposphere.

The photodissociation of carbon tetrachloride occurs also in the stratosphere, according to the absorption cross section values as measured by *Molina and Rowland* [1975] and a photolysis study by *Davis et al.* [1975]. The dominant photochemical process should be at relatively low pressure, according to *Jayanty et al.* [1975*a*].

$$(d_{1f_1}) \qquad CCl_4 + h\nu \rightarrow CCl_2 + Cl_2 \qquad (161a)$$
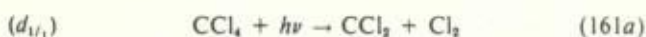
and at high pressure the process

$$(d_{1f_2}) \qquad CCl_4 + h\nu \rightarrow CCl_3 + Cl \qquad (161b)$$

may occur.

Other fluorocarbons should also be studied; but an exact knowledge of their ultraviolet absorption spectrum is also required in order to determine the atmospheric region (stratosphere, mesosphere, or thermosphere) where photodissociation can occur. A recent survey by C. Sandorfy (unpublished manuscript, 1975) shows that the photchemical behavior in the stratosphere of the various fluorocarbons depends on the number of chlorine (and bromine) atoms. Molecules like CH$_3$Cl [*Russell et al.*, 1973] and other chloromethanes must be studied with their photodissociation processes and subsequent reactions in the stratosphere.

A detailed analysis of the various Cl productions, after the release of the first atom in the direct photolysis step, is required for each compound CFCl$_3$, CF$_2$Cl$_2$, and CCl$_4$ in order to determine the vertical distribution of the secondary chlorine compounds in the stratosphere.

When a chlorine atom is produced, it reacts immediately with stratospheric ozone, the result being chlorine monoxide:

$$(d_2) \qquad Cl + O_3 \rightarrow ClO + O_2 + 39 \text{ kcal} \qquad (162a)$$
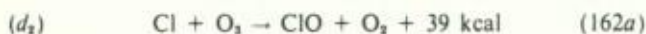
with a rate coefficient (D. D. Davis and R. T. Watson, private communication, 1975)

$$d_2 = (3.6 \pm 0.4) \times 10^{-11} e^{-318 \pm 50 /T} \text{ cm}^3 \text{ s}^{-1} \qquad (162b)$$

between 220 and 298 K.

The ClO radical is subject to two rapid bimolecular reactions in the stratosphere:

$$(d_3) \qquad ClO + O \rightarrow Cl + O_2 + 55 \text{ kcal} \qquad (163a)$$
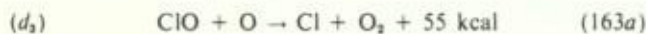
with a reported rate coefficient [*Bemand et al.*, 1973]

$$d_3 = 5.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (163b)$$

and

$$(d_4) \qquad ClO + NO \rightarrow Cl + NO_2 + 9 \text{ kcal} \qquad (164a)$$
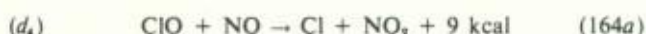
with a rate coefficient [*Clyne and Watson*, 1974]

$$d_4 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (164b)$$

When a chlorine atom is produced, it may react by

bimolecular reactions with various stratospheric molecules such as CH$_4$, H$_2$, HO$_2$, H$_2$O$_2$, and HNO$_3$.

The first reaction, which has been considered by *Molina and Rowland* [1974*a*], *Stolarski and Cicerone* [1974], and *Wofsy and McElroy* [1974], is

$$(d_5) \qquad Cl + CH_4 \rightarrow CH_3 + HCl + 0.6 \pm 2.4 \text{ kcal} \qquad (165a)$$
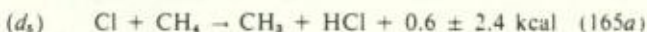
for which the rate coefficient has been measured between 218 and 350 K by D. D. Davis and R. T. Watson (private communication, 1975) as

$$d_5 = (5.0 \pm 0.5) \times 10^{-12} e^{-1114 \pm 38 /T} \text{ cm}^3 \text{ s}^{-1} \qquad (165b)$$

The reaction with molecular hydrogen

$$(d_6) \qquad Cl + H_2 \rightarrow H + HCl - 1 \text{ kcal} \qquad (166a)$$

leads to $d_6 = 1.4 \times 10^{-14}$ at 298 K [*Davis et al.*, 1970] and does not yet lead to a well-defined value of the activation energy. A working value between 195 and 496 K [*Clyne and Walker*, 1973] can be adopted.

$$d_6 = 5.6 \times 10^{-11} e^{-2250 /T} \text{ cm}^3 \text{ s}^{-1} \qquad (166b)$$

No laboratory measurements have been made for the reaction of Cl with HO$_2$, H$_2$O$_2$, and HNO$_3$, and values that have been used [*Wofsy and McElroy*, 1974; *Crutzen*, 1974*b*; *Molina and Rowland*, 1975] are estimates obtained by comparison with other reactions:

$$(d_7) \qquad Cl + HO_2 \rightarrow O_2 + HCl + 46 \text{ kcal} \qquad (167a)$$

with

$$d_7 = 1 \times 10^{-11} \text{ to } 10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (167b)$$

and

$$(d_8) \qquad Cl + H_2O_2 \rightarrow HCl + HO_2 + 16 \text{ kcal} \qquad (168a)$$
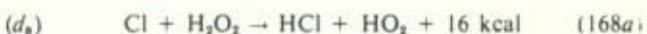
with the value of the rate coefficient assumed to be [*Molina and Rowland*, 1975]

$$d_8 = 10 \times a_{30} \qquad (168b)$$

i.e., 10 times the rate coefficient of OH with H$_2$O$_2$.

In addition,

$$(d_9) \qquad Cl + HNO_3 \rightarrow HCl + NO_3 + 2 \text{ kcal} \qquad (169a)$$

also with the value of the rate coefficient assumed to be [*Molina and Rowland*, 1975]

$$d_9 = 10 \times b_{27} \qquad (169b)$$

i.e., 10 times the rate coefficient of OH with HNO$_3$.

Hydrogen chloride molecules, which are formed by all the reactions (165) to (169), but particularly by reaction (165), may react in a bimolecular process such as

$$(d_{10}) \qquad HCl + O \rightarrow Cl + OH - 1 \text{ kcal} \qquad (170a)$$

with a rate coefficient [*Brown and Smith*, 1975] of

$$d_{10} = 5 \times 10^{-13} e^{-2450/T} \text{ cm}^3 \text{ s}^{-1} \qquad (170b)$$

The other reaction which plays a role at stratospheric level is

$$(d_{11}) \qquad HCl + OH \rightarrow Cl + H_2O + 16 \text{ kcal} \qquad (171a)$$
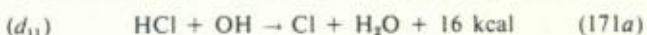
for which there are excellent laboratory measurements over a large range of temperatures (213–478 K) *Smith and Zellner* [1974] and *Zahnizer et al.* [1974] leading to an average value

$$d_{11} = 3 \times 10^{-12} e^{-400/T} \text{ cm}^3 \text{ s}^{-1} \qquad (171b)$$

If we consider the first 10 reactions ((161)–(171)) involving simple chlorine compounds with the various production processes by photodissociation ((159)–(160)), we may write for chlorine monoxide:

$$n(ClO)[J_{ClO} + d_3n(O) + d_4n(NO)] = d_2n(Cl)n(O_3) \quad (172)$$

since $dn(ClO)/dt = 0$ in stratospheric conditions where $d_3n(O) + d_4n(NO) > 10^{-3}$ s^{-1}. It is therefore possible to deduce the ratio $n(ClO)/n(Cl)$ and to determine the concentration of chlorine atoms by

$$n(Cl)[d_2n(O_3) + d_5n(CH_4) + d_6n(H_2)$$

$$+ d_7n(HO_2) + d_8n(H_2O_2) + d_9n(HNO_3)]$$

$$= n(HCl)[J_{HCl} + d_{10}n(O) + d_{11}n(OH)]$$

$$+ n(Cl_2)J_{Cl_2} + n(ClO)J_{ClO} + n(CFCl_3)J_{CFCl_3}$$

$$+ n(CF_2Cl_2)J_{CF_2Cl_2} + n(CCl_4)J_{CCl_4} + \cdots \quad (173)$$

since $d_2n(O_3) > 10^{-1}$ s^{-1} in the stratosphere. Thus the practical equation for the determination of the Cl concentrations is

$$n(Cl)d_2n(O_3) = P(Cl) \quad (174)$$

where $P(Cl)$ involves all possible production processes of chlorine atoms.

Hydrogen chloride cannot be considered to attain a steady state in the stratosphere. The equation governing the rate of change of the concentration $n(HCl)$ is

$$\frac{dn(HCl)}{dt} + n(HCl)[J_{HCl} + d_{10}n(O) + d_{11}n(OH)]$$

$$= n(Cl)[d_5n(CH_4) + d_6n(H_2) + d_7n(HO_2)$$

$$+ d_8n(H_2O_2) + d_9n(HNO_3)] \quad (175)$$

It is not possible to write conditions for the day equilibrium, since all terms, J_{HCl}, $d_{10}n(O)$, and $d_{11}n(OH)$, are too small, as can be seen when the numerical values of the various parameters involved are introduced. In fact, transport must be involved, and the form which must be normally used in studies of the stratosphere for HCl is

$$\frac{\partial n(HCl)}{\partial t} + \text{div } [n(HCl)w(HCl)]$$

$$+ n(HCl)[J_{HCl} + d_{10}n(O) + d_{11}n(OH)]$$

$$= n(Cl)[d_5n(CH_4) + d_6n(H_2) + a_7n(HO_2)$$

$$+ d_8n(H_2O_2) + d_9n(HNO_3)] \quad (176)$$

for which the lower boundary conditions must play an important role near the tropopause, since a rapid removal occurs by tropospheric rainout. Thus hydrogen chloride should lead to the normal loss process of stratospheric chlorine. Observations are required therefore at various latitudes above the tropopause; at the present time, measurements have been made only by *Lazrus et al.* [1975], who found an increase of the HCl mixing ratio from the tropopause of less than 10^{-10} to about 4×10^{-10} above 25 km.

The catalytic removal of ozone by chlorine compounds occurs by the simultaneous action of

$$(d_2) \qquad\qquad Cl + O_3 \rightarrow ClO + O_2 \qquad\qquad (162)$$

and

$$(d_3) \qquad\qquad ClO + O \rightarrow Cl + O_2 \qquad\qquad (163)$$
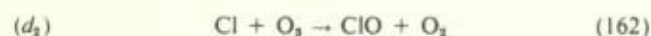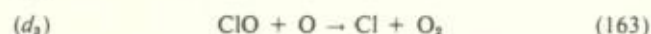
which is counterbalanced at lower levels by

$$(d_4) \qquad\qquad ClO + NO \rightarrow Cl + NO_2 \qquad\qquad (164)$$
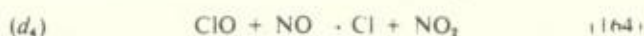
Thus the additional terms to be added to the general equation governing the rate of the concentration $n(O_3)$ in the stratosphere are

$$\frac{\partial n(O_3)}{\partial t} + \text{div } [n(O_3)w(O_3)] + \cdots$$

$$+ n(O_3) d_2n(Cl) + n(O)d_3n(ClO) = P(O) \quad (177)$$

where $P(O)$ represents the various production processes (see equation (150)). If we introduce condition (172) in (177), this equation can conveniently be written:

$$\frac{\partial n(O_3)}{\partial t} + \text{div } [n(O_3)w(O_3)] + \cdots + 2n(O_3)d_2n(Cl)$$

$$= P(O) + n(ClO)[J_{ClO} + d_4n(NO)] \quad (178)$$

The form shown in (178) and illustrated in Figure 11 indicates how chlorine atoms lead to the removal of stratospheric ozone. A concentration of chlorine atoms of the order of 5×10^8 leads to a loss rate of $2 \times 10^{-5}n(O_3)$ cm^{-3}s^{-1}. However, when the Cl concentration is reduced to less than 10^8 cm^{-3}, the lifetime of an ozone molecule is still of the order of a year. On the other hand, the production term $d_4n(NO)n(ClO)$ must be considered, since, for ClO concentrations of the order of 10^7 or 10^8 cm^{-3}, it leads to a production process of odd oxygen of not less than 10^5 or 10^6 cm^{-3}s^{-1}, respectively. In other words, the effect of nitric oxide on chlorine monoxide is to reduce the action of the catalytic cycle involving Cl with O (162) and ClO with O (163) which removes odd oxygen from the stratosphere. Thus a detailed analysis with exact rate coefficients is still required before the aeronomic behavior of Cl compounds can be determined with enough accuracy. The concentrations of hydrogen and nitrogen compounds should be known, at least within a factor of 2, and at present the complexity of the chlorine-nitrogen-hydrogen-oxygen atmosphere gives only a general indication of the situation. Reliance cannot yet be placed on precise quantitative features such as the exact percentage of reduction of stratospheric ozone.

Before ending this preliminary analysis of the chlorine processes, it must be pointed out that the action of ClO on NO (reaction (163)) must be compared with the action of O_3 on NO (reaction (94)). The best approximation (96) to the ratio $n(NO_2)/n(NO)$ should be modified if ClO plays a role and
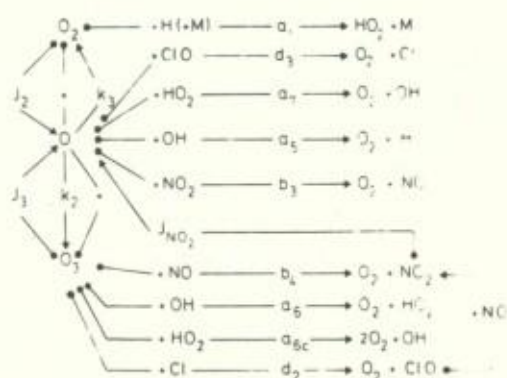
Fig. 11. General reaction scheme in which are simultaneously involved the chlorine, nitrogen, and hydrogen radicals (atoms or molecules) related directly to the production and loss of odd oxygen in the stratosphere.

would then be written

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2 n(O) + b_4 n(O_3) + d_4 n(ClO)}{J_{NO_2} + b_3 n(O)} \quad (179)$$

or, in the major part of the stratosphere,

$$\frac{n(NO_2)}{n(NO)} = \frac{b_4 n(O_3) + d_4 n(ClO)}{J_{NO_2}} \quad (180)$$

With a concentration $n(ClO) \geq 5 \times 10^6$ cm^{-3}, it is possible to write

$$d_4 n(ClO) \geq b_4 n(O_3) \quad (181)$$

i.e., that the ratio $n(NO_2)/n(NO)$, which is well-defined in a nitrogen-oxygen stratosphere, may change in a chlorine-nitrogen-oxygen atmosphere, the indication being that there is a strong interaction between ClO_x and NO_x cycles in addition to the interaction with the HO_x cycle.

If we extend the chlorine oxide radical chemistry to chlorine peroxide and trioxide, other reactions must be introduced:

(d_{12}) $\qquad$ Cl + O$_2$ + M $\rightarrow$ ClOO + M $\qquad$ (182a)
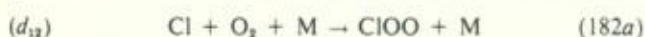
with, at temperatures between 200 and 300 K [*Clyne and Coxon*, 1968],

$$d_{12} = 5.5 \times 10^{-34} n(M) \text{ cm}^3 \text{ s}^{-1} \quad (182b)$$

A calculation by *Watson* [1974] gives the variation with height of the reverse reaction

(d_{12r}) $\qquad$ ClOO + M $\rightarrow$ Cl + O$_2$ + M $\qquad$ (182c)
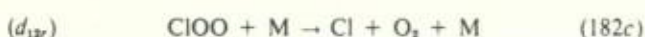
d_{12r} increases from 2×10^{-17} cm^3 s^{-1} in the lower stratosphere to about 10^{-15} at the stratopause level.

We may also have [according to *Simonaitis and Heicklen*, 1975b]

(d_{13}) $\qquad$ Cl + O$_3$ + O$_2$ $\rightarrow$ ClO$_3$ + O$_2$ $\qquad$ (183a)
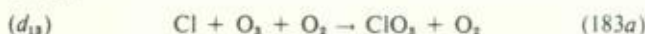
where, at 300 K,

$$d_{13} = (4 \pm 2) \times 10^{-30} n(O_2) \text{ cm}^3 \text{ s}^{-1} \quad (183b)$$

The reaction between ClO and O$_3$ leads to

(d_{14}) $\qquad$ ClO + O$_3$ $\rightarrow$ ClOO + O$_2$ $\qquad$ (184a)

$\qquad\qquad$ ClO + O$_3$ $\rightarrow$ OClO + O$_2$ + 33 kcal

where at 298 K [*Davis et al.*, 1973d],

$$d_{14} \leq 5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \quad (184b)$$

The photodissociation of ClOO occurs only at $\lambda < 300$ nm

(d_{15}) $\qquad$ ClOO + $h\nu(\lambda < 268$ nm) $\rightarrow$ ClO + O $\qquad$ (185)

and can exist only in the stratosphere. The photodissociation of OClO at $\lambda > 300$ nm

(d_{16}) $\qquad$ OClO + $h\nu(\lambda < 375$ nm) $\rightarrow$ ClO + O $\qquad$ (186)

is related to a predissociation process that occurs at greater wavelengths than the dissociation continuum ($\lambda < 276$ nm). The reactions of OClO with O and NO are as follows:

(d_{17}) $\qquad$ OClO + O $\rightarrow$ ClO + O$_2$ + 61 kcal $\qquad$ (187a)

where [*Bemand et al.*, 1973]

$$d_{17} = 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad (187b)$$

and

(d_{18}) $\qquad$ OClO + NO $\rightarrow$ ClO + NO$_2$ + 15 kcal $\qquad$ (188a)
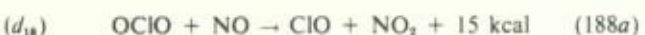
where [*Bemand et al.*, 1973]

$$d_{18} = 3.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad (188b)$$

On the other hand, the photodissociation of ClO$_3$ leads to

(d_{19}) $\qquad$ ClO$_3$ + $h\nu(\lambda < 350$ nm) $\rightarrow$ ClO + O$_2$ $\qquad$ (189)

$\qquad\qquad$ ClO$_3$ + $h\nu(\lambda < 350$ nm) $\rightarrow$ OClO + O
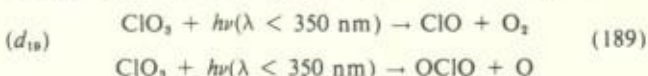
This process leads to a rapid photodissociation [*Simonaitis and Heicklen*, 1975b] if the absorption cross sections by *Goodeve and Richardson* [1937] are used. However, according to *Simonaitis and Heicklen* [1975b], the production of perchloric acid must be considered:

(d_{20}) $\qquad$ ClO$_3$ + OH $\rightarrow$ HClO$_4$ $\qquad$ (190a)
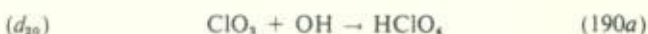
with a rate coefficient which could be of the order of

$$d_{20\infty} = 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \quad (190b)$$

leading to a possible removal of stratospheric chlorine.

In addition to the reactions which should be introduced for a discussion of compounds such as ClO$_2$ and ClO$_3$ (reactions (182) to (190)), other reactions may be considered. However, the role they play cannot be compared with those of all processes, (162) to (190), which have been discussed. A list is given without any discussion even when the reaction is rapid:

(d_{21}) $\qquad$ H + OClO $\rightarrow$ OH + ClO $\qquad$ (191)

(d_{22}) $\qquad$ H + HCl $\rightarrow$ H$_2$ + Cl $\qquad$ (192)

(d_{23}) $\qquad$ H + Cl$_2$ $\rightarrow$ HCl + Cl $\qquad$ (193)

(d_{24}) $\qquad$ Cl + Cl + M $\rightarrow$ Cl$_2$ + M $\qquad$ (194)

(d_{25a}) $\qquad$ Cl + ClOO $\rightarrow$ 2ClO $\qquad$ (195a)

(d_{25b}) $\qquad$ Cl + ClOO $\rightarrow$ Cl$_2$ + O$_2$ $\qquad$ (195b)

(d_{26}) $\qquad$ Cl + OClO $\rightarrow$ 2ClO $\qquad$ (196)

(d_{27}) $\qquad$ ClO + ClO $\rightarrow$ Cl + OClO $\qquad$ (197)

(d_{28a}) $\qquad$ ClO + ClO $\rightarrow$ Cl + ClOO $\qquad$ (198a)

(d_{28b}) $\qquad$ ClO + ClO $\rightarrow$ Cl$_2$ + O$_2$ $\qquad$ (198b)

(d_{29}) $\qquad$ ClO + ClO + M $\rightarrow$ Cl$_2$ + O$_2$ + M $\qquad$ (199)
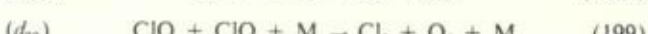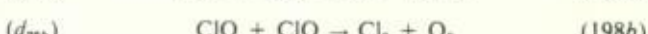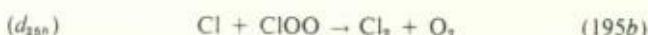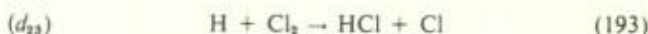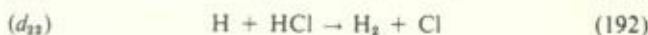
Finally, reactions [*Sandoval et al.*, 1974; *Pitts et al.*, 1974; *Jayanty et al.*, 1975a, b] such as

(d_{30a}) $\qquad$ O(^1D) + CCl$_4$ $\rightarrow$ CCl$_3$ + ClO $\qquad$ (200a)

(d_{30b}) $\qquad$ O(^1D) + CFCl$_3$ $\rightarrow$ CFCl$_2$ + ClO $\qquad$ (200b)
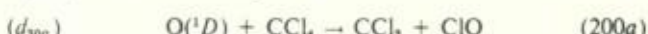
may be considered. Values of the rate coefficient d_{30} are of the order of $(3 \pm 1) \times 10^{-10}$ cm^3 s^{-1}. There is therefore a very small effect on the atmospheric sink of fluorocarbons. In addition, the reactions (with their exact activation energies) of the various halocarbons with the hydroxyl radicals should also be considered with their various products in order to know the exact tropospheric and stratospheric sinks. For example, a lifetime of a year (to reduce the halocarbon concentration to 50% of its value) requires a rate coefficient of about 5×10^{-14} cm^3 s^{-1} if the OH concentration is of the order of 10^6 cm^3 s^{-1} (daytime, ground level at 300 K). In the lower stratosphere the lifetime would be of the order of 5 yr when OH has the same concentration.

At the present time, there are still other possibilities of chlorine intrusion into the stratosphere [*Cicerone et al.*, 1975].

TABLE 2. Basic Reactions Involved in the Determination of the Ozone Concentration in the Stratosphere

Oxygen Atmosphere

Equation Number	Reaction	Rate Coefficient
	$O_2 + h\nu \rightarrow O + O$	(J_2)
	$O_3 + h\nu \rightarrow O + O_2$	(J_3)
	$O_3 + h\nu(\lambda < 310) \rightarrow O(^1D) + O_2$	$(J_3{}^*)$
(2)	$O + O_2 + M \rightarrow O_3 + M$	(k_2)
(3)	$O + O_3 \rightarrow 2O_2$	(k_3)

Hydrogen-Oxygen Atmosphere

Equation Number	Reaction	Rate Coefficient
(11)	$H + O_2 + M \rightarrow HO_2 + M$	(a_1)
(12)	$H + O_3 \rightarrow OH + O_2$	(a_2)
(15)	$O + OH \rightarrow H + O_2$	(a_5)
(17)	$O + HO_2 \rightarrow O_2 + OH$	(a_7)
(16)	$OH + O_3 \rightarrow HO_2 + O_2$	(a_6)
(16)	$HO_2 + O_3 \rightarrow OH + 2O_2$	(a_{6c})
	For Ratio $n(OH)/n(HO_2)$	
(129)	$NO + HO_2 \rightarrow OH + NO_2$	$(a_{26}), (b_{29})$
(56)	$CO + OH \rightarrow H + CO_2$	(a_{26})
	For Production of OH	
(29)	$O(^1D) + H_2O \rightarrow OH + OH$	(a_{12})
(44)	$O(^1D) + H_2 \rightarrow H + OH$	(a_{24})
(61)	$O(^1D) + CH_4 \rightarrow CH_3 + OH$	(c_1)
(62)	$OH + CH_4 \rightarrow CH_3 + H_2O$	(c_2)
(64)	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	(c_4)
(65)	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	(c_5)
(76)	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	(c_{16})
(67)	$H_2CO + h\nu \rightarrow HCO + H \rightarrow CO + 2HO_2$	(c_{7a})
(67)	$H_2CO + h\nu \rightarrow H_2 + CO$	(c_{7b})
	For Loss of OH	
(34)	$OH + HO_2 \rightarrow O + H_2O$	(a_{17})
(127)	$OH + HNO_3 \rightarrow NO_3 + H_2O$	(b_{27})

Nitrogen-Hydrogen-Oxygen Atmosphere

Equation Number	Reaction	Rate Coefficient
(93)	$O + NO_2 \rightarrow NO + O_2$	(b_3)
(94)	$O_3 + NO \rightarrow NO_2 + O_2$	(b_4)
(95)	$NO_2 + h\nu \rightarrow NO + O$	(b_5)
	For Production and Loss of Nitrogen Oxides	
(122)	$NO_2 + OH + M \rightarrow HNO_3 + M$	(b_{22})
(135)	$HNO_3 + h\nu \rightarrow OH + NO_2$	(J_{HNO_3})
(110)	$NO_2 + h\nu \rightarrow NO_3 + O$	(J_{NO_2})

Chlorine-Nitrogen-Hydrogen-Oxygen Atmosphere

Equation Number	Reaction	Rate Coefficient
(162)	$Cl + O_3 \rightarrow ClO + O_2$	(d_2)
(163)	$ClO + O \rightarrow Cl + O_2$	(d_3)
(164)	$ClO + NO \rightarrow Cl + NO_2$	(d_4)
	For Production and Loss of HCl	
(165)–(169)	$Cl + CH_4, \cdots \rightarrow HCl + \cdots$	$(d_5)–(d_9)$
(170)	$O + HCl \rightarrow Cl + OH$	(d_{10})
(171)	$OH + HCl \rightarrow Cl + H_2O$	(d_{11})

For example, an estimate with the present effect of CF_2Cl_2, $CFCl_3$, and CCl_4 could lead to a mixing ratio of the order of 4×10^{-10} for ClX (Cl + HCl + ClO) at and above the ozone peak. According to the same authors, a ground level source of 2.6×10^8 chloromethane molecules cm^{-2} s^{-1} with an upward flux of 1.7×10^8 cm^{-2} s^{-1} at the 15-km level would lead, with this additional effect, to a total ClX mixing ratio not far from 10^{-9}, i.e., 8×10^{-10} above 30 km. Such conditions correspond to a constant mixing ratio of CH_3Cl at ground level of 4×10^{-10} with a possible abstraction reaction involving OH [*Cicerone et al.*, 1975] with various subsequent reactions [*Sanhueza and Heicklen*, 1975]. Furthermore, very recent observations (December 1974 to April 1975) by *Lovelock* [1975] lead to a mean mixing ratio of the order of 10^{-9}. Such a high concentration of chloromethane with a corresponding tropospheric lifetime of 0.37 yr, according to *Lovelock* [1975] indicates that it is the most important stratospheric chlorine source produced by the biosphere.

In conclusion, if the mixing ratio of odd chlorine tends to reach 10^{-9}, a very precise analysis is required, since the efficiency for ozone depletion by the mechanism $d_2n(Cl)n(O_3)$ cm^{-3} s^{-1} must be considered at the present time in the upper stratosphere (>35 km), where the mechanism $d_4n(ClO)n(NO)$ cm^{-3} s^{-1} cannot counterbalance its effects, as it can in the lower stratosphere (equation (172)). A Cl concentration greater than 5×10^4 cm^{-3} and reaching 10^5 cm^{-3} would lead to ozone removal according the mechanism $2d_2n(Cl)n(O_3)$ cm^{-3} s^{-1}, which will compete with the mechanisms $2b_3n(O)n(NO_2)$ and $2a_5n(O)n(OH)$ in the upper stratosphere and at the stratopause level, respectively.

Finally, it can be said that in the development of a simple chemical system for describing the ozone distribution in the stratosphere, a minimum number of reactions is needed. Table 2 shows the principal reactions which cannot be omitted. Furthermore, in addition to these reactions, which are presented under successive headings for a pure oxygen atmosphere and that atmosphere with the added effects of hydrogen compounds, of nitrogen compounds, and of chlorine compounds, it is necessary to introduce the production processes of molecular hydrogen, the various mechanisms which lead to nitric oxide in the stratosphere, and the dissociation processes of Freons, carbon tetrachloride, and chloromethane which give chlorine atoms. Finally, departures from chemical equilibrium conditions must be taken into account, particularly for H_2 and CH_4, NO and HNO_3, and HCl, for which transport plays a role. It should be noted that it is not sufficient to consider steady state conditions even involving transport in the lower stratosphere, since variations of the tropopause are very important.

SOLAR RADIATION

Our knowledge of solar radiation in the ultraviolet which plays a role in the photodissociation of molecular oxygen is due to rocket and balloon data. At wavelengths longer than 240 nm the solar brightness temperature is generally greater than 5000 but less than 6000 K. The solar constant is of the order of 1.95 ± 0.01 cal cm^{-2} min^{-1} or 136 ± 1 mW cm^{-2} [*Labs and Neckel*, 1971; *Thekaekara*, 1973; *Willson*, 1973]. which corresponds to an effective temperature of the order of 5770 ± 10 K. This temperature is the absolute temperature T_e of a black body derived from the Stefan-Boltzmann equation corresponding to the case in which Planck's law is applied to the whole spectrum:
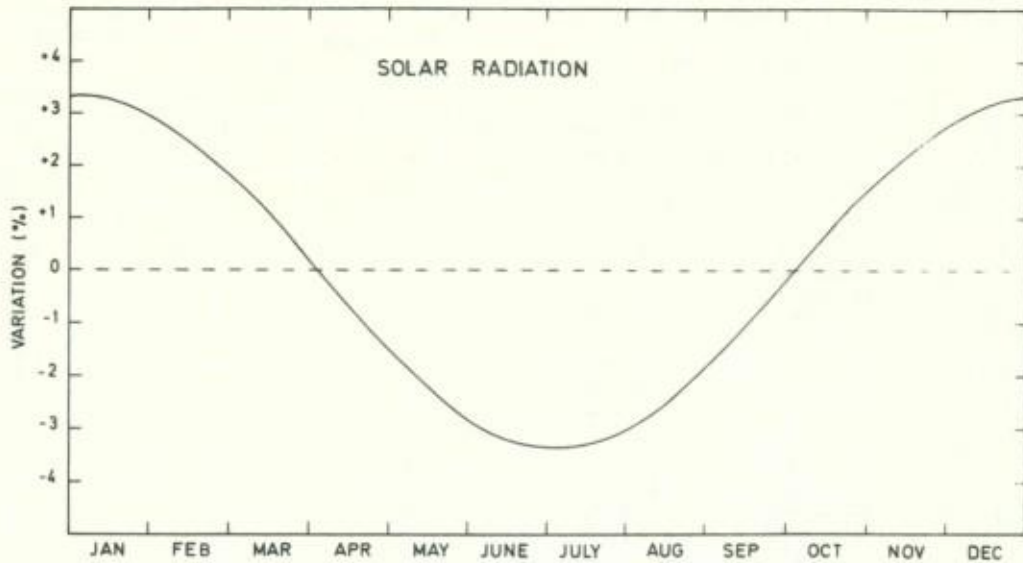
Fig. 12. Variation (in percent) of the solar flux corresponding to the variation of the sun-to-earth distance: variations are 6.6% between the first week of January and the first week of July.

$$\rho_\beta(\nu) = \frac{8\pi h\nu^3}{c^3} (e^{h\nu/kT_S} - 1)^{-1} \qquad (201)$$

where $\rho_N(\nu)$ is the radiation density of frequency ν; $h = 6.626 \times 10^{-27}$ erg s, Planck constant; $k = 1.381 \times 10^{-16}$ erg K^{-1}, Boltzmann constant; and $c = 2.9979 \times 10^{10}$ cm s^{-1}, velocity of light.

At the top of the earth's atmosphere the radiation density $\rho_N(\nu)$ is reduced by the dilution factor β_N:

$$\beta_N = R^2/4r^2 = 5.4 \times 10^{-6} \qquad (202)$$

where R represents the solar radius and r denotes the mean earth-to-sun distance. The variation with the earth-to-sun distance is shown in Figure 12 and corresponds to $\pm3.3\%$. The maximum occurs in the first week of January and leads to

$$\beta_S(\text{max}) = 5.59 \times 10^{-6} \qquad (202a)$$

while the minimum occurs 6 months later in the first week of July

$$\beta_S(\text{min}) = 5.23 \times 10^{-6} \qquad (202b)$$

There is therefore a variation of 6.6% every 6 months in the solar flux reaching the top of the terrestrial atmosphere. The average value is reached during the first week of April and November. Such a variation of the solar flux must be taken into account when variations of the order of 10% or less are considered in aeronomic processes. In fact, the solar constant at the top of the earth's atmosphere corresponds to the maximum value of 2.01 cal cm^{-2} min^{-1} in January and to the minimum value of 1.88 cal cm^{-2} min^{-1} in July.

As we go down the wavelength scale from 290 to 250 nm the brightness temperature decreases from 5500 to 5000 K (see

TABLE 3. Solar Flux in the Spectral Region of the Herzberg Continuum of O_2

Number[*]	$\Delta\nu$, cm^{-1}	λ, nm	q, cm^{-2} s^{-1}
58	50,500–51,000	196.1–198.0	1.01×10^{12}
59	50,000–50,500	198.0–200.0	1.20×10^{12}
60	49,500–50,000	200.0–202.0	1.44×10^{12}
61	49,000–49,500	202.0–204.1	1.80×10^{12}
62	48,500–49,000	204.1–206.2	2.08×10^{12}
63	48,000–48,500	206.2–208.3	2.45×10^{12}
64	47,500–48,000	208.3–210.5	5.09×10^{12}
65	47,000–47,500	210.5–212.8	7.12×10^{12}
66	46,500–47,000	212.8–215.0	9.23×10^{12}
67	46,000–46,500	215.0–217.4	8.42×10^{12}
68	45,500–46,000	217.4–219.8	1.20×10^{13}
69	45,000–45,500	219.8–222.2	1.22×10^{13}
70	44,500–45,000	222.2–224.7	1.77×10^{13}
71	44,000–44,500	224.7–227.3	1.60×10^{13}
72	43,500–44,000	227.3–229.9	1.96×10^{13}
73	43,000–43,500	229.9–232.6	1.97×10^{13}
74	42,500–43,000	232.6–235.3	1.70×10^{13}
75	42,000–42,500	235.3–238.1	2.00×10^{13}
76	41,500–42,000	238.1–241.0	1.77×10^{13}
77	41,000–41,500	241.0–243.9	2.58×10^{13}

Photons cm^{-2} s^{-1} for $\Delta\nu = 500$ cm^{-1} at the top of the earth's atmosphere for mean sun-to-earth distance. Solar flux data from 58 to 72 are based on those of *Simon* [1974b] and from 73 to 77 on those of *Broadfoot* [1972].

[*] Nomenclature used by *Ackerman* [1971].

Fig. 13. Number of photons available at the top of the terrestrial atmosphere for the mean sun-to-earth distance between 244 and 196 nm. Values in cm^{-2} s^{-1} for $\Delta\nu = 500$ cm^{-1} as given in Table 3

TABLE 4. Solar Flux in the Spectral Region of the Hartley Bands of O_3

Number[*]	$\Delta\nu$, cm^{-1}	$\Delta\lambda$, nm	q, cm^{-2} s^{-1}
77	41,000–41,500	241.0–243.9	2.58×10^{13}
78	40,500–41,000	243.9–246.9	2.35×10^{13}
79	40,000–40,500	246.9–250.0	2.38×10^{13}
80	39,500–40,000	250.0–253.2	2.28×10^{13}
81	39,000–39,500	253.2–256.4	3.24×10^{13}
82	38,500–39,000	256.4–259.7	5.83×10^{13}
83	38,000–38,500	259.7–263.2	4.89×10^{13}
84	37,500–38,000	263.2–266.7	1.19×10^{14}
85	37,000–37,500	266.7–270.3	1.29×10^{14}
86	36,500–37,000	270.3–274.0	1.17×10^{14}
87	36,000–36,500	274.0–277.8	1.11×10^{14}
88	35,500–36,000	277.8–281.7	7.85×10^{13}
89	35,000–35,500	281.7–285.7	1.50×10^{14}
90	34,500–35,000	285.7–289.9	2.12×10^{14}
91	34,000–34,500	289.9–294.1	3.56×10^{14}
92	33,500–34,000	294.1–298.5	3.33×10^{14}
93	33,000–33,500	298.5–303.0	3.08×10^{14}
94	32,500–33,000	303.0–307.7	4.39×10^{14}

Photons cm^{-2} s^{-1} for $\Delta\nu$ = 500 cm^{-1} at the top of the earth's atmosphere for mean sun-to-earth distances. Solar flux data from 90 to 94 are based on those of *Simon* [1974] and from (77) to (93) on those of *Broadfoot* [1972].
  * Nomenclature used by *Ackerman* [1971].

TABLE 5. Solar Flux in the Spectral Region of the Huggins Bands of O_3 and Photodissociation Continuum of NO_2

Number[*]	λ, nm	q, cm^{-2} s^{-1}
95	310	4.95×10^{14}
96	315	5.83×10^{14}
97	320	6.22×10^{14}
98	325	6.96×10^{14}
99	330	8.61×10^{14}
100	335	8.15×10^{14}
101	340	8.94×10^{14}
102	345	8.44×10^{14}
103	350	8.69×10^{14}
104	355	9.14×10^{14}
105	360	8.23×10^{14}
106	365	1.07×10^{15}
107	370	1.08×10^{15}
108	375	9.72×10^{14}
109	380	1.11×10^{15}
110	385	8.98×10^{14}
111	390	1.18×10^{15}
112	395	9.34×10^{14}
113	400	1.69×10^{15}
114	405	1.70×10^{15}

Photons cm^{-2} s^{-1} for $\Delta\lambda$ = 5 nm (50 Å) at the top of the earth's atmosphere. Solar flux data are derived from those of *Arvesen et al* [1969] and reduced to a solar constant value of 1.95 cal cm^{-2} min^{-1}.
  * Nomenclature used by *Ackerman* [1971].

Ackerman [1971] and references therein for a general description of the solar spectrum to be used in the study of the photodissociation of molecular oxygen and ozone). The brightness temperature falls to about 4500 K in the spectral range of the Schumann-Runge continuum of O_2 [*Ackerman and Simon, 1973; Rottman, 1974*]. An analysis of Rottman's data shows that the maximum temperature occurs in the spectral range 175–170 nm with T = 4550 K; the brightness temperature reaches only 4450 K [*Parkinson and Reeves, 1969; Brueckner and Moe, 1972; Carver et al., 1972; Nishi, 1973; Nishi et al., 1974; Jordan and Ridgeley, 1974*] in the spectral range of 155–165 nm, which is the region of the lowest temperature. Since the brightness temperature between 175 and 130 nm is T = 4525 ± 25 K, the photodissociation of molecular oxygen in the Schumann-Runge continuum can be computed with an average black-body temperature of the order of 4525 K.

It is convenient to compute the solar emission in terms of photons cm^{-2} s^{-1} available at the top of the terrestrial atmosphere. The number of photons of frequency ν, $q(\nu)$, is given, from (1), by

$$q(\nu) = \frac{c\beta_s \rho_s(\nu)}{h\nu} = \frac{8\pi\beta_s\nu^2}{c^2} (e^{h\nu/kT} - 1)^{-1} \qquad (203)$$

leading to a total number of photons, Q, available at frequencies greater than ν,

$$Q = \int_\nu^\infty q(\nu)\, d\nu = \frac{8\pi\beta_s}{c^2} \left(\frac{kT}{h}\right)^3 \int_x^\infty \frac{x^2\, dx}{e^x - 1} \qquad (204)$$

where $x = h\nu/kT$.

Since $e^{h\nu/kT_s}$ is appreciably greater than 1, the integrated relation (204) can be written in a simplified form for numerical calculation in a spectral range ν_1–ν_2:
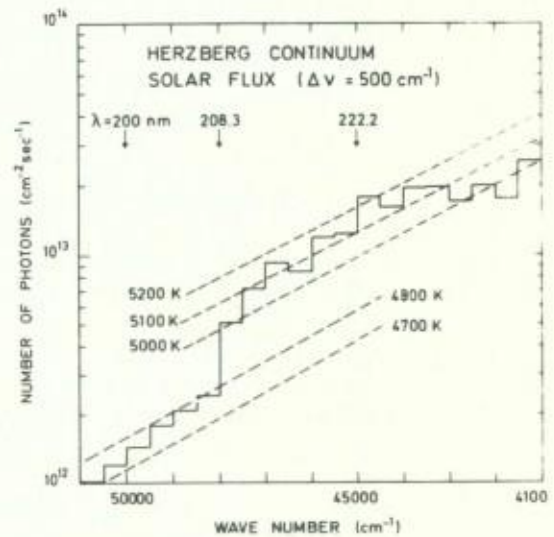

Fig. 14. Number of photons available at the top of the terrestrial atmosphere for the mean sun-to-earth distance between 241 and 308 nm. Values in cm^{-2} s^{-1} for $\Delta\nu$ = 500 cm^{-1} as given in Table 4.
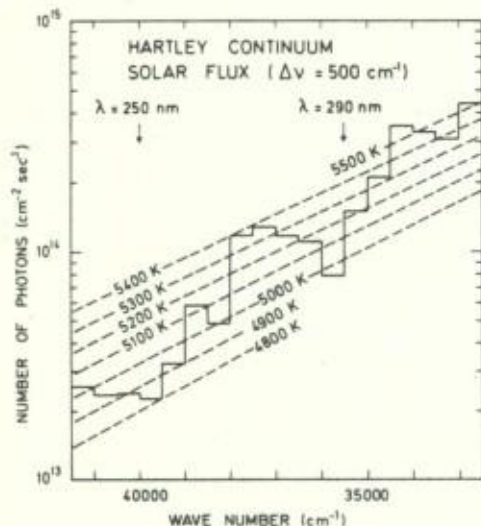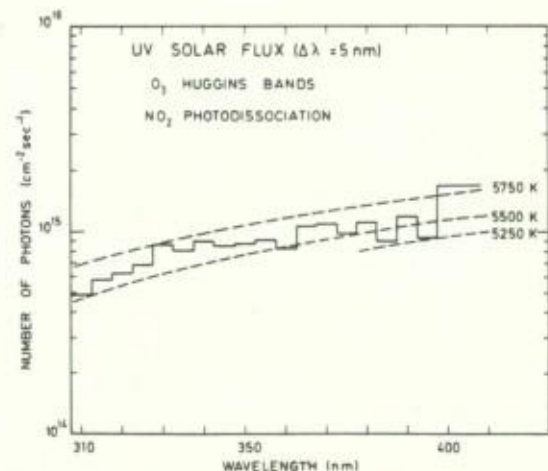

Fig. 15. Number of photons available at the top of the terrestrial atmosphere for the mean sun-to-earth distance between 310 and 400 nm. Values in cm^{-2} s^{-1} for $\Delta\lambda$ = 5 nm as given in Table 5.

TABLE 6. Solar Flux in the Visible Part of the Spectrum

Number*	λ, nm	q†
113	400	1.69
114	405	1.70
115	410	1.84
116	415	1.97
117	420	1.95
118	425	1.81
119	430	1.67
120	435	1.98
121	440	2.02
122	445	2.18
123	450	2.36
124	455	2.31
125	460	2.39
126	465	2.38
127	470	2.39
128	475	2.44
129	480	2.51
130	485	2.30
131	490	2.39
132	495	2.48
133	500	2.40
134	505	2.46
135	510	2.49
136	515	2.32
137	520	2.39
138	525	2.42
139	530	2.55
140	535	2.51
141	540	2.49
142	545	2.55
143	550	2.53
144	555	2.54
145	560	2.50
146	565	2.57
147	570	2.58
148	575	2.67
149	580	2.67
150	585	2.70
151	590	2.62
152	595	2.69
153	600	2.63
154	605	2.68
155	610	2.66
156	615	2.59
157	620	2.69
158	625	2.61
159	630	2.62
160	635	2.62
161	640	2.63
162	645	2.60
163	650	2.55
164‡	655	2.48
165	660	2.57
166	665	2.61
167	670	2.61
168	675	2.62
169	680	2.62
170	685	2.57
171	690	2.52
172	695	2.60
173	700	2.58
174	705	2.52
175	710	2.51
176	715	2.48
177	720	2.45
178	725	2.48
179	730	2.45
180	735	2.44
181	740	2.39
182	745	2.40
183	750	2.41
184	755	2.40
185	760	2.38
186	765	2.34

TABLE 6 (continued)

Number*	λ, nm	q†
187	770	2.32
188	775	2.30
189	780	2.33
190	785	2.34
191	790	2.29
192	795	2.29
193	800	2.27

Solar flux data derived from those of Table 7 of *Arvesen et al.* [1969] and reduced to a solar constant value of 1.95 cal cm⁻² min⁻¹.

*Nomenclature used by *Ackerman* [1971].

†Here $q = 10^{-11}$ photons cm⁻² s⁻¹ for $\Delta\lambda = 5$ nm at the top of the terrestrial atmosphere for mean sun-to-earth distance. $\lambda \pm 2.5$ nm.

‡Extension of nomenclature.

$$Q(\nu_1 - \nu_2) = \frac{8\pi\beta_s}{c^2}\left(\frac{kT}{h}\right)\left\{e^{-h\nu/kT}\left[\left(\frac{h\nu}{kT} + 1\right)^2 + 1\right]\right\}_{\nu_2}^{\nu_1} \tag{205}$$

The rocket or balloon data, when transformed into photon flux intensities, are readily converted in this way into brightness temperatures showing how much the radiation level used for aeronomic purposes has varied since 1950. A low temperature ($T = 4500$ K) in the Schumann-Runge continuum was used by *Nicolet and Mange* [1954], who adopted the average value observed by *Friedman et al.* [1951] near 150 nm using photon counters. Other values were adopted later [*Detwiler et al.*, 1961; *Hinteregger et al.*, 1965] leading to a solar flux at the top of the terrestrial atmosphere of about 2.7×10^{12} photons cm⁻² s⁻¹ in the Schumann-Runge continuum, which corresponds to a brightness temperature of 4900 K. A reduction of not less than 200 K was introduced by *Ackerman* [1971] corresponding to a flux of only 1.3×10^{12} photons. However, recent measurements by *Ackerman and Simon* [1973] and *Rottman* [1974] lead to another decrease for the adopted value of the solar flux; the number of solar photons available at the top of the earth's atmosphere in the spectral range of the Schumann-Runge continuum must be of the order of 6.3×10^{11} cm⁻² s⁻¹, corresponding to a brightness temperature of only 4525 ± 25 K, which must be introduced in aeronomic calculations of thermospheric problems.

In the spectral region of the Schumann-Runge bands (200-175 nm) the absolute values of the solar radiation flux are not well-known. Between 185 and 195 nm the spectrum is not yet well-known, so that it is not certain how the brightness temperature goes from 4500 to 4700 K [see *Donnelly and Pope*, 1973]. However, an indication has been given by *Ackerman* [1974] in his analysis of the aeronomic problem of the δ bands of nitric oxide. In the spectral range of the NO lines in the δ(1 − 0) band ($\Delta\lambda = 182 - 183$ nm), the brightness temperature is 4580 K, as was observed by *Rottman* [1974], and between 190.5 and 192.5 nm in the spectral range of the NO lines in the δ(0 − 0) band the brightness temperature increases up to 4660 K.

Below 185 nm, the number of photons has been measured recently [*Rottman*, 1974]; it corresponds to $T = 4550 \pm 50$ K. For wavelengths longer than 195 nm, a recent analysis by *Simon* [1974a] shows an increase of brightness temperatures up to 4700 K at 196 nm and about 4800 K at the discontinuity in the continuum flux near 209 nm [*Boland et al.*, 1971] which is due to the photoionization edge of AlI.

Since there is an important decline of the brightness temperature between 200 and 190 nm [*Widing et al.*, 1970],

TABLE 7. Standard Atmosphere, Latitude 45°

Altitude, km	Temperature, K	Scale Height, km	Pressure, mbar	Concentration, cm^{-3}	Total, cm^{-2}
0	288	8.44	1013	2.55×10^{19}	2.15×10^{25}
5	256	7.50	540	1.53×10^{19}	1.15×10^{25}
10	223	6.56	265	8.60×10^{18}	5.64×10^{24}
15	217	6.37	121	4.05×10^{18}	2.58×10^{24}
20	217	6.38	55	1.85×10^{18}	1.18×10^{24}
25	222	6.54	25	8.33×10^{17}	5.45×10^{23}
30	227	6.69	12	3.82×10^{17}	2.56×10^{23}
35	237	7.00	5.7	1.76×10^{17}	1.23×10^{23}
40	250	7.42	2.9	8.31×10^{16}	6.17×10^{22}
45	264	7.84	1.5	4.09×10^{16}	3.21×10^{22}
50	271	8.05	0.8	2.14×10^{16}	1.72×10^{22}

new, precise absolute measurements are needed between 180 and 200 nm in order to determine with precision the vertical structure of the photodissociation of molecular oxygen in the mesosphere where the absorption of the Schumann-Runge bands plays the leading role and also of various minor constituents of the upper stratosphere which are photodissociated in this spectral region.

In the spectral range of the Herzberg continuum of molecular oxygen, which is absorbed in the stratosphere simultaneously by O_2 and O_3, the solar flux has been measured several times [*Ackerman*, 1971]. Recent measurements by *Simon* [1974b] and *Broadfoot* [1972] can be used between 196 and 242.4 nm and are reproduced in Table 3 for $\Delta \nu = 500$ cm^{-1}. Figure 13 exhibits the observed and computed values for various brightness temperatures between 4700 and 5200 K. The strong discontinuity near 208.7 nm is revealed by the transition from 4800 to 5000 K in the brightness temperature. It is clear that the solar flux in the Herzberg continuum must be divided into two parts corresponding to radiation of about 4750 ± 50 K and 5100 ± 100 K, respectively.

The spectral region of the solar spectrum corresponding to the Hartley continuum, where ozone absorbs solar radiation in the stratosphere, has been given with intensities at 0.1-nm intervals by *Broadfoot* [1972]. Recent values obtained by *Simon* [1974b] for $\Delta \lambda = 285-308$ nm are in good agreement ($\pm 5\%$) with Broadfoot's data. The number of photons $cm^{-2} s^{-1}$ for $\Delta \nu = 500$ cm^{-1} are given in Table 4. The spectrum has been plotted in Figure 14 with the curves for various solar brightness temperatures between 4800 and 5500 K.

Many observations have been made in the spectral region ($\lambda > 310$ nm) of the solar ultraviolet flux transmitted to the ground. Differences between spectra measured by various investigators have been recently discussed by *DeLuisi* [1975]. His own results are in agreement with the data of *Arvesen et al.* [1969] for $\lambda > 310$ nm. Considering the results obtained by *Broadfoot* [1972] in the spectral region $\Delta \lambda = 350-320$ nm, by *Simon* [1974] between 300 and 350 nm, by *Arvesen et al.* [1969] for $\lambda > 300$ nm, and by *Thekaekara* [1974] in his solar spectral irradiance standard curve, it seems possible to describe the solar spectrum for $\Delta \lambda = 5$ nm between 300 and 400 nm with an error which may reach 10% in certain intervals. Adopted values are provided in Table 5. In the overlapping region of Simon's and Arvesen's data (310-350 nm) the average difference (after a shift of 4 Å in Arvesen's data) is -2%, corresponding to the difference of the total irradiances which were used: 1.99 cal cm^{-2} min^{-1} instead of 1.95 cal cm^{-2} min^{-1}. The values used for $\Delta \lambda = 5$ nm are about 10% lower than data tabulated by *Ackerman* [1971]; they are shown in Figure 15 and correspond to solar fluxes equivalent to brightness temperatures between 5500 and 5750 K, except in two spectral ranges with strong absorption in the solar spectrum at $\lambda = 385 \pm 2.5$ nm and $\lambda = 395 \pm 2.5$ nm (Ca, K, and H lines), where the brightness temperature is only about 5250 K. For a more detailed spectrum, very precise observational data are needed [see *DeLuisi*, 1975], and shifts in the wavelengths of the spectrum must be avoided; see discussions by *Broadfoot* [1972], *Simon* [1974b], and *DeLuisi* [1975] concerning *Arvesen*'s [1969] and *Thekaekara*'s [1974] spectra.

In the visible part of the spectrum we adopt the same procedure as used for the 310- to 400-nm spectral region, and the numerical results, which can be used for the calculation of photodissociation coefficients, are given in Table 6 for a spectral interval of 5 nm. For a more detailed calculation, for example for $\Delta \lambda = 0.1$ nm, a specific analysis is required, special attention being given to the exact wavelength and the absolute solar flux.

TABLE 8. Standard Atmosphere, Latitude 45°: Constituents

Altitude, km	$n(N_2)$, cm^{-3}	$N(N_2)$, cm^{-2}	$n(O_2)$, cm^{-3}	$N(O_2)$, cm^{-2}	$n(O_3)$, cm^{-3}	$N(O_3)$, cm^{-2}
0	1.99×10^{19}	1.68×10^{25}	5.34×10^{18}	4.50×10^{24}	9.0×10^{11}	1.03×10^{19}
5	1.20×10^{19}	8.96×10^{24}	3.21×10^{18}	2.40×10^{24}	6.8×10^{11}	9.91×10^{18}
10	6.71×10^{18}	4.40×10^{24}	1.80×10^{18}	1.18×10^{24}	1.3×10^{12}	9.50×10^{18}
15	3.16×10^{18}	2.01×10^{24}	8.48×10^{17}	5.41×10^{23}	2.8×10^{12}	8.44×10^{18}
20	1.44×10^{18}	9.21×10^{23}	3.87×10^{17}	2.47×10^{23}	5.2×10^{12}	6.42×10^{18}
25	6.50×10^{17}	4.25×10^{23}	1.75×10^{17}	1.14×10^{23}	4.5×10^{12}	3.89×10^{18}
30	2.99×10^{17}	2.00×10^{23}	8.02×10^{16}	5.37×10^{22}	3.1×10^{12}	2.01×10^{18}
35	1.37×10^{17}	9.61×10^{22}	3.69×10^{16}	2.58×10^{22}	1.6×10^{12}	8.46×10^{17}
40	6.49×10^{16}	4.81×10^{22}	1.74×10^{16}	1.29×10^{22}	6.7×10^{11}	2.94×10^{17}
45	3.19×10^{16}	2.50×10^{22}	8.56×10^{15}	6.71×10^{21}	2.1×10^{11}	9.25×10^{16}
50	1.67×10^{16}	1.34×10^{22}	4.47×10^{15}	3.60×10^{21}	7.0×10^{10}	2.85×10^{16}

Concentrations denoted by n and totals by N.

TABLE 9. Absorption Coefficients of O_2 and O_3 for $\Delta\nu = 500$ cm^{-1} [Ackerman, 1971] in the Herzberg Continuum

Number	$\Delta\nu$	$\sigma(O_2)$, cm^2	$\sigma(O_3)$, cm^2
77	41,000–41,500	6.74×10^{-25}	9.00×10^{-18}
76	41,500–42,000	1.75×10^{-24}	7.97×10^{-18}
75	42,000–42,500	2.44×10^{-24}	6.86×10^{-18}
74	42,500–43,000	3.09×10^{-24}	5.79×10^{-18}
73	43,000–43,500	3.76×10^{-24}	4.83×10^{-18}
72	43,500–44,000	4.40×10^{-24}	4.00×10^{-18}
71	44,000–44,500	5.03×10^{-24}	3.24×10^{-18}
70	44,500–45,000	5.65×10^{-24}	2.55×10^{-18}
69	45,000–45,500	6.28×10^{-24}	1.97×10^{-18}
68	45,500–46,000	6.92×10^{-24}	1.52×10^{-18}
67	46,000–46,500	7.60×10^{-24}	1.17×10^{-18}
66	46,500–47,000	8.28×10^{-24}	8.57×10^{-19}
65	47,000–47,500	8.93×10^{-24}	6.26×10^{-19}
64	47,500–48,000	9.55×10^{-24}	4.84×10^{-19}
63	48,000–48,500	1.00×10^{-23}	4.11×10^{-18}
62	48,500–49,000	1.05×10^{-23}	3.51×10^{-19}
61	49,000–49,500	1.14×10^{-23}	3.26×10^{-18}
60	49,500–50,000	1.5×10^{-23}	3.26×10^{-19}
59	50,000–50,500	2.0×10^{-23}	3.30×10^{-18}
58	50,500–51,000	3.0×10^{-23}	3.69×10^{-19}

ATMOSPHERIC PARAMETERS

The atmospheric properties of the stratosphere cannot be studied without the use of a certain number of tables representing basic quantities such as total pressure, temperature, and concentrations of the principal constituents. Furthermore, since the purpose of a detailed analysis of the stratosphere is to take into account increased knowledge in the ozone distribution and in the detection of important trace constituents, the principal observational results must be considered.

The U.S. Standard Atmosphere (1962) can be used as a basis for the principal parameters. Table 7 gives numerical values which can be adopted. In particular, when a mixing ratio is given, a reference should be given to an atmospheric model in order to establish the exact concentrations. It is also convenient to present for this standard atmosphere numerical values which can be taken as references for different types of variation. These values are given in Table 8 where the various proportions are as follows: N_2, 0.7808; O_2, 0.2095; Ar, 0.0093. The ozone distribution which has been adopted is based on rocket measurements published by Krueger [1973] and sounding balloon measurements published by Hering and Borden [1965]. As the standard atmospheric model, this ozone distribution does not represent all conditions but can be taken as a model in order to avoid too speculative conclusions If the absorption cross sections as presented by Ackerman [1971] and reproduced in Table 9 are used, it can be shown by means of the solar fluxes of Table 2 that the photodissociation of O_2 in the stratosphere is essentially due to the solar radiation of $\lambda > 190$ nm. At 50 km, at the stratopause as illustrated in Figure 16, the major part (80%) of the atomic oxygen production for overhead sun conditions occurs by absorption of the solar radiation of $\lambda > 195$ nm. When the penetration of solar radiation in the stratosphere occurs the important part of the spectrum corresponds to the region centered at 210 nm between 220 and 200 nm. For overhead sun conditions the atomic oxygen production for $\lambda > 195$ nm is 85% at 40 km, 87% at 35 km, 91% at 30 km, and 96% at 25 km. When high precision is required for the photodissociation rate of molecular oxygen at the stratopause and in the upper stratosphere, the predissociation in the Schumann-Runge bands must be introduced. Furthermore, when the photodissociation of minor constituents depends on the solar radiation at $\lambda < 200$ nm, it is necessary to introduce the effect of the rotational structure of the Schumann-Runge bands as shown in Figure 17.

In order to facilitate visualization of the behavior of the O_3 and O_2 absorption in the stratosphere, curves illustrative of this absorption are shown in Figure 18. Molecular oxygen is the major absorbing molecule at the stratopause level, but ozone plays the leading role in the mean stratosphere (25–30 km). Thus the photodissociation of molecular oxygen is related to the vertical distribution of ozone and its variations.

Another important aspect is the vertical distribution of the atomic oxygen production; it is illustrated in Figure 19 where various percentages are shown versus the solar zenith angle. More than 50% is always produced above 40 km, where photoequilibrium conditions can be accepted. On the other hand, almost the total production (97.5%) occurs above 25 km, i.e., above the ozone peak. There is therefore no doubt that the stratospheric ozone below its concentration peak is essentially due to a downward transport from the production regions Figure 20 is another illustration of this distribution of the ozone formation resulting from the atomic oxygen production with a peak in the upper stratosphere between 40 and 50 km The production at 20 km is not more than 0.1%, even for overhead sun conditions.

Under these standard conditions it is also possible to derive the time necessary to produce the ozone concentration as given in Table 6. The variation with altitude changes as depicted in Figure 21. Above 40 km, it always requires less than a day; at 25 km, the times are not less than 1 month for continuous overhead sun conditions and reach a year for sec $\chi = 2$, i.e., for a sun altitude of 30°. Below the ozone peak, at 20 km, more than 2 years would be necessary to produce the observed ozone, and transport must be substituted for production.

A standard model cannot represent the atmospheric conditions in the stratosphere. The U.S. Standard Atmosphere Supplements (1966) show the departures of temperatures and pressures of atmospheres at 30°, 45°, 60°, and 75°N (winter and summer) from the standard atmosphere given in Table 5.
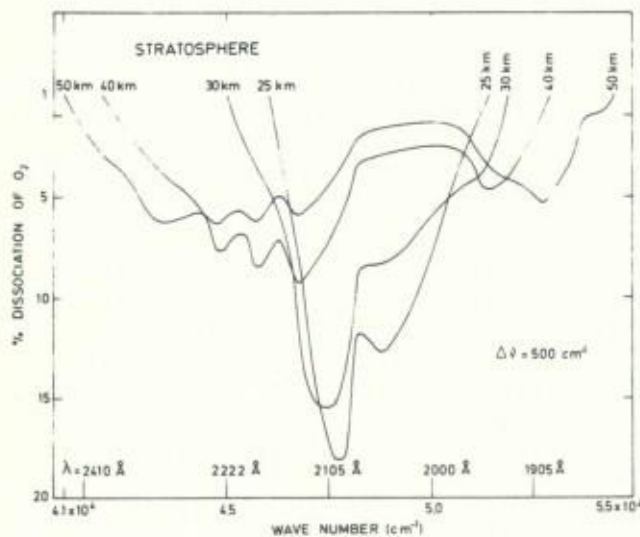

Fig. 16. Dissociation of molecular oxygen in the stratosphere according to the wavelength for various heights from the stratopause to 25 km for overhead sun conditions. The percentages are given for the spectral range $\Delta\nu = 500$ cm^{-1}; standard conditions prevail.
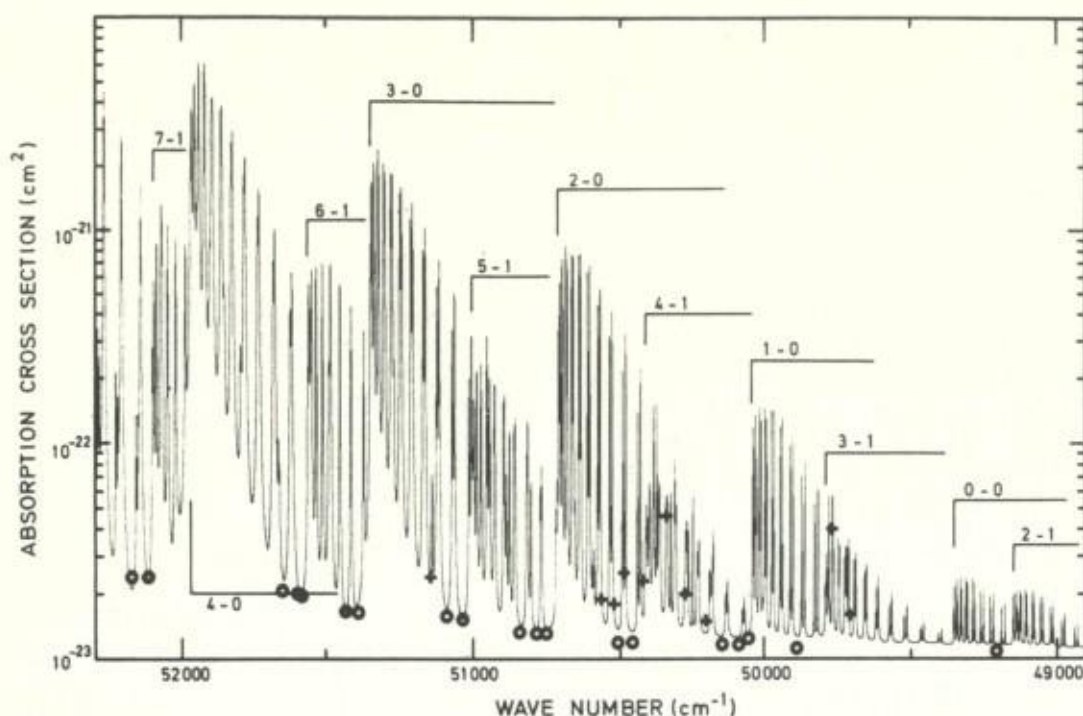
Fig. 17. Rotational structure of the Schumann-Runge bands of O_2 at 300 K [*Ackerman et al.*, 1970] from (0 – 0) to (7–1). Theoretical determination with laboratory data are indicated by crosses, and with experimental continuum by *Ogawa* [1971] by circles. Effect of the Herzberg continuum is important for $\nu < 51,000$ cm^{-1}.

The temperature-altitude profiles indicate that the important differences occur between 10 and 20 km; they are related to the height of the tropopause and have therefore an effect on the rate coefficients in the lower stratosphere. It is not the intention to reproduce here the various atmospheric parameters concerning the principal constituents. However, it is useful to mention that there is an isothermal layer in the U.S. Standard Atmosphere (1972) from 11 to 20 km with a temperature equal to 216.65 K. In the Supplementary Atmospheres (1966), there is large variation in the tropopause temperature with altitude for summer and winter conditions from latitude 15° to 75°. However, if latitude and temperature are to be considered, their variation must be taken into account when lower boundary conditions are introduced into the calculation of strato-

spheric models. Figures 22 and 23 show the extent of the stratospheric regions with tropical or polar tropopauses. The extreme limits reached by the polar tropopause in January in the northern hemisphere (Figure 22) are about 10° in Africa, while the tropical tropopause reaches 40° over the Mediterranean Sea. The curve (50%) is an indication of the geographic regions where the number of observations of tropical and polar tropopauses is the same. In the summertime (Figure 23), there is an extension of the stratospheric regions with tropical tropopause toward the northern latitudes. Such differences must be introduced in the study of the behavior of the lower stratosphere when only the mean height is required. However, it is clear from the position of the three curves of Figures 22 and 23 that there is a considerable variability which must be considered. An example deduced from a recent analysis by *Downie* [1974] is illustrated by the various curves in Figure 24, which give the number of occurrences at various latitudes of the tropopause height. The scatter is the principal picture of the winter tropopause for latitudes larger than 30°. The high tropical tropopause (Miami, 26°N, for example) is well-defined. Thus the climatological aspect is not sufficient to assess the atmospheric conditions of the lower stratosphere, and it is necessary to consider synoptic conditions. It is not possible to refer to all publications on the subject, but a study by means of vertical cross sections given by *Piaget* [1971] leads to an analysis of the ozone exchanges between the stratosphere and troposphere. An example of a vertical profile from tropical to polar regions is given in Figure 25, where various tropopauses are shown. The fact that this atmospheric situation is associated with the problem of the jet stream reveals that the problem of the lower stratosphere cannot be studied with steady state conditions and with constant lower boundary condition. Another indication is given by the vertical cross section illustrated by Figure 26, where a specific ozone increase is indicated by three conventional tropopauses in the latitude
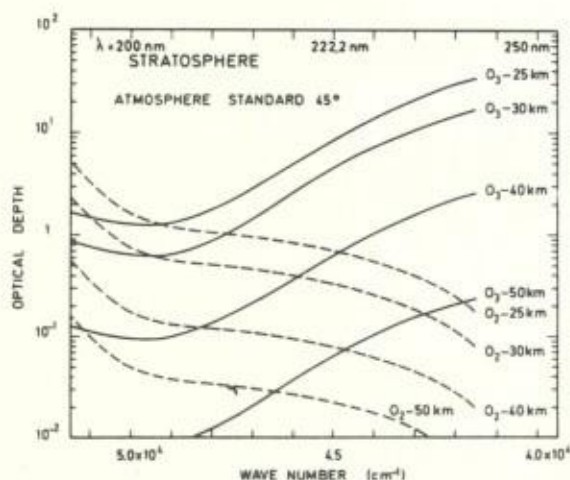

Fig. 18. Optical depth of molecular oxygen and ozone absorption in the stratosphere in the spectral region leading to O_2 dissociation at various heights.
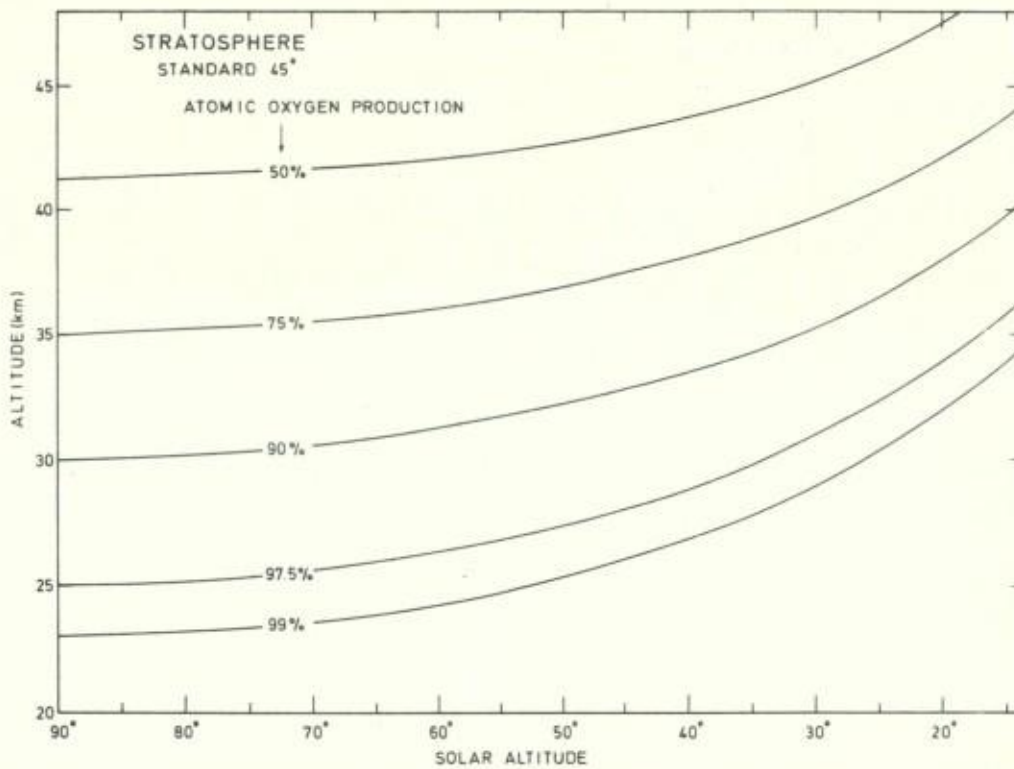
Fig. 19. Total atomic oxygen production (percentage) for various altitudes of the sun: an overhead sun is from $h_S = 90°$ to $h_S = 20°$.

range of less than 10°. The stratospheric air intrusion in the troposphere is related to the jet stream by various kinds of transport from advection to more complicated dynamic effects. A schematic view of the various exchanges between the lower stratosphere and troposphere is depicted by Figure 27, in which the projection of isentropic trajectories is reported in the meridian plane perpendicular to the jet stream axis. The principal inversions corresponding to various frontal surfaces and tropopauses are shown by shading. The outline of the trajectories, after sporadic intrusions into the tropopause due to strong convective motions, indicates the motions of the tropical stratospheric air (denoted by *a*) and of the tropical tropospheric air (denoted by *b*), which travel toward the jet stream latitudes (indicated by *c*) above the conventional tropopause. The region, which is indicated by *d* in Figure 27, corresponds to the subtropical jet stream. The intrusions of polar stratospheric air into the troposphere are illustrated by *e*, which corresponds to a normal flow, and by *f*, which shows an additional effect associated with the penetration of polar air inside of the cold air. Finally, it should be noted how the ozone mixing ratio is related to the various air motions. If the variations of the vertical distribution of ozone and of its total amount are associated with the tropopause behavior, the seasonal and latitudinal variations cannot be omitted. A diagram of the annual variation of total ozone for various latitudes is shown in Figure 28. The continuous curves represent conditions for which all abnormalties have been averaged out. At mean and high latitudes there is a very large variation with maximum during winter and spring and with minimum during summer and autumn. As is clearly indicated in Figure 29, the highest total amounts of ozone occur in the Arctic regions during the spring, while the lowest values are observed in the tropical region during the whole year. It is interesting to see (Figure 28) how the total amount increases during the

winter months in the high-latitude region when there is no ozone production. An illustration of the ozone production is given by Figure 30, where the annual variation at various latitudes is shown. At the equator the total production of atomic oxygen or ozone formation, which is $(1.4 \pm 0.1) \times 10^{18}$ atoms or molecules cm^{-2} day^{-1}, is practically constant during the year. At 45° there is a strong variation from about 3×10^{17} molecules cm^{-2} day^{-1} in January to 1.6×10^{18} molecules cm^{-2} day^{-1} in June–July. At latitudes greater than 60° the winter production is negligible. There is therefore no direct associa-
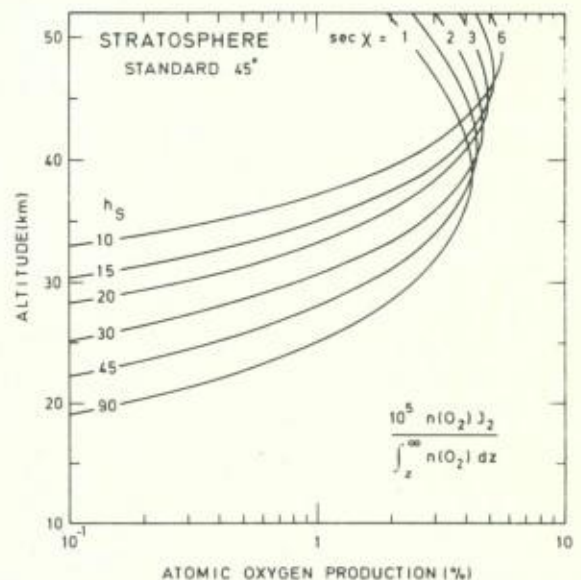

Fig. 20. Vertical distribution of the atomic oxygen production (percentage) for various altitudes of the sun; $h_s = 90°$, overhead sun. A layer of 1-km thickness is considered.
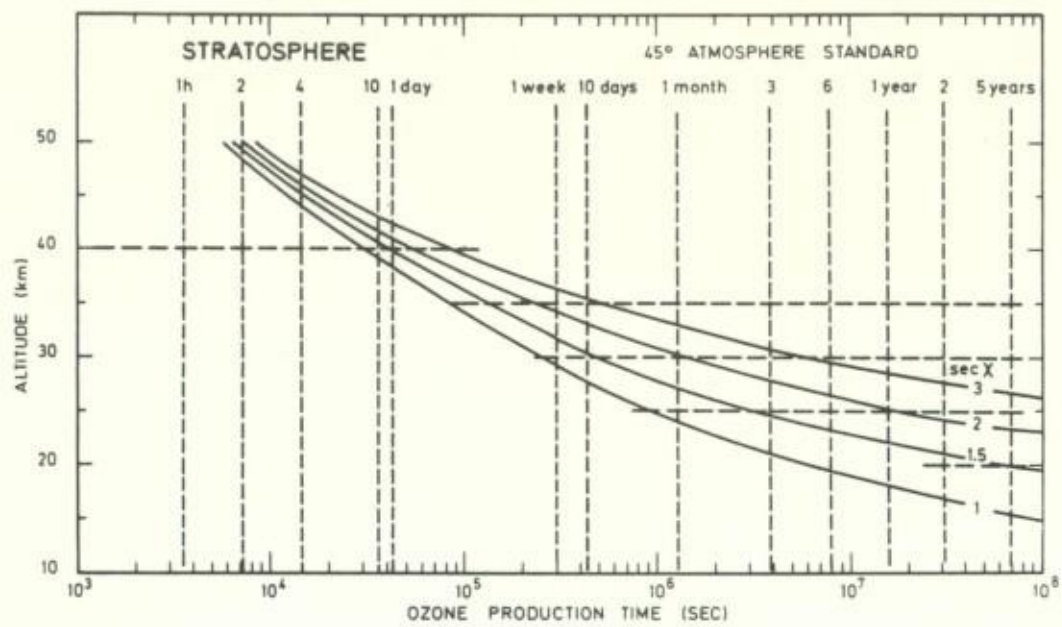
Fig. 21.   Production times of stratospheric ozone (concentrations given in Table 8) for various solar zenith angles
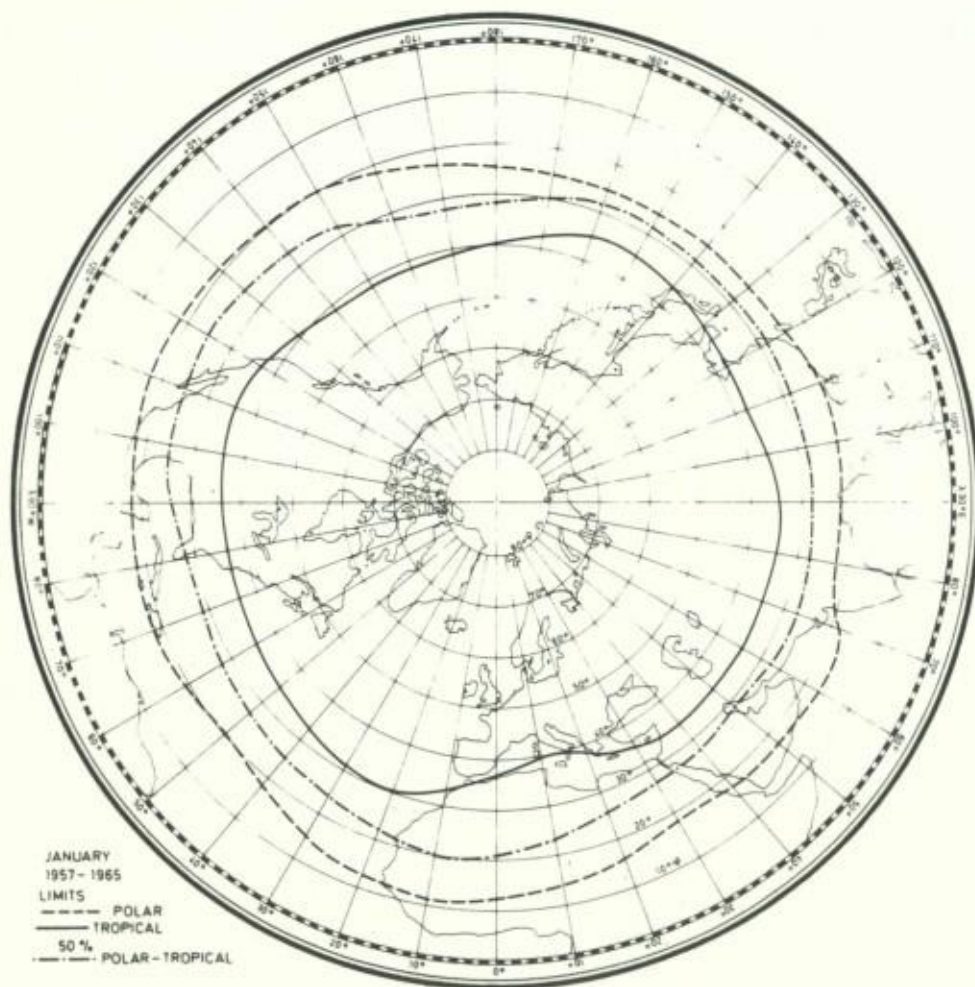

Fig. 22.   Limits of the lower stratospheric regions indicated by the geographic distribution of the polar and tropical tropopauses in January (1957–1965) in the northern hemisphere [*Makhover*, 1972].
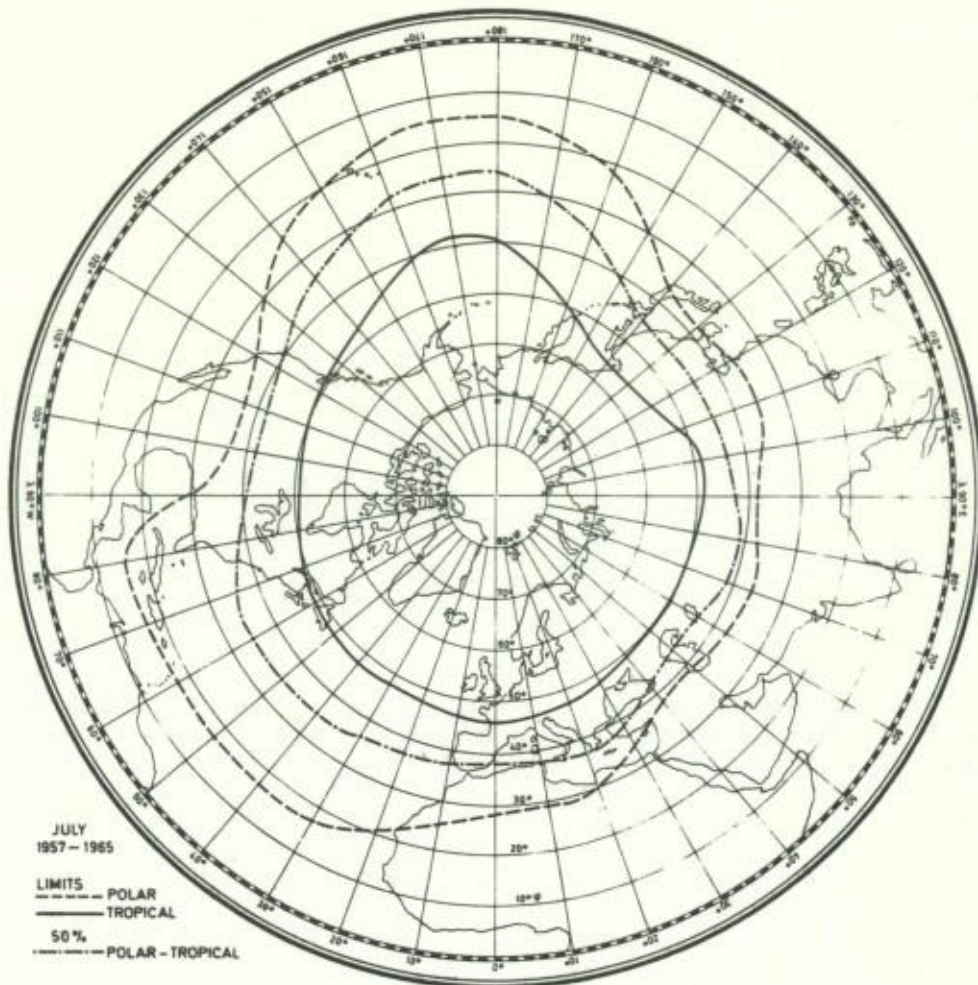
Fig. 23. Limits of the lower stratospheric regions indicated by the geographic distribution of the polar and tropical tropopauses in July (1957–1965) in the northern hemisphere [*Makhover*, 1972].
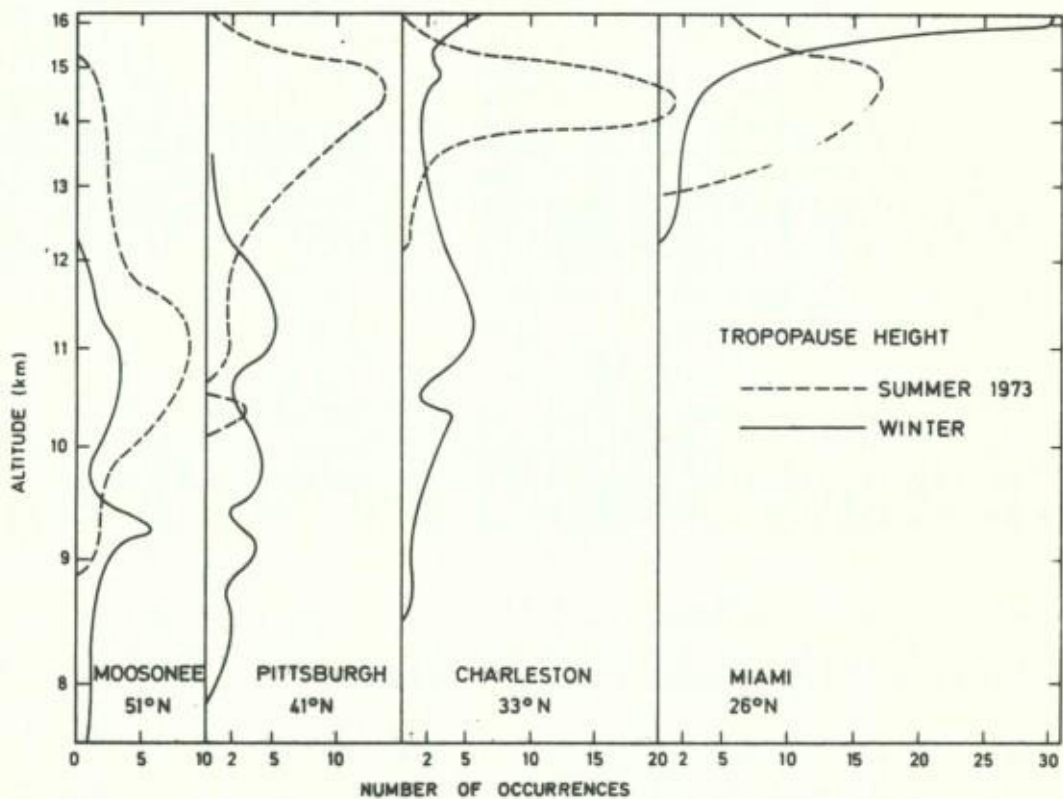

Fig. 24. Variations of tropopause heights for summer and winter conditions at four stations between 21° and 51°N [*Downie*, 1974].
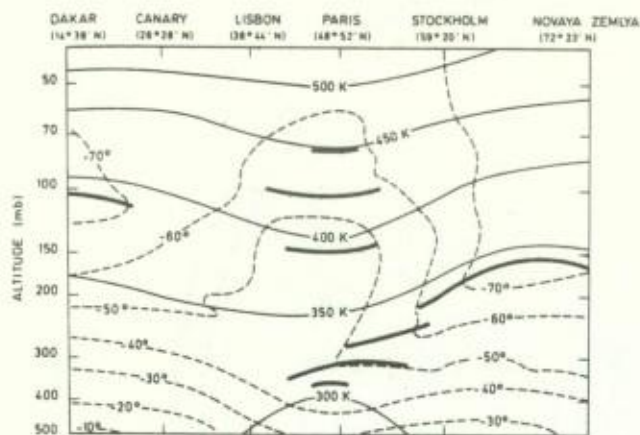
Fig. 25. Vertical profiles from tropical regions to the polar regions, February 17, 1967, 0000 UT, from *Piaget* [1971]. Isentropic lines are in K, and isothermal lines are in °C. The various conventional tropopauses are indicated by heavy lines. Details are given by *Piaget* [1971].

tion between the seasonal and latitudinal distribution of ozone and its production. Its total amount is maximum where and when it is not produced. A complete explanation by transport requires not only air motions from the production region to the polar stratosphere during about 3 months in order to explain the winter increase but also, if chemical action is not possible, the general decrease from spring to summer. Recent analyses by *Dobson* [1973a, b] and *Dütsch* [1974], which consider particularly the air movements associated with ozone transport in the lower stratosphere, reveal the complexity of the ozone vertical distribution with various kinds of variations.
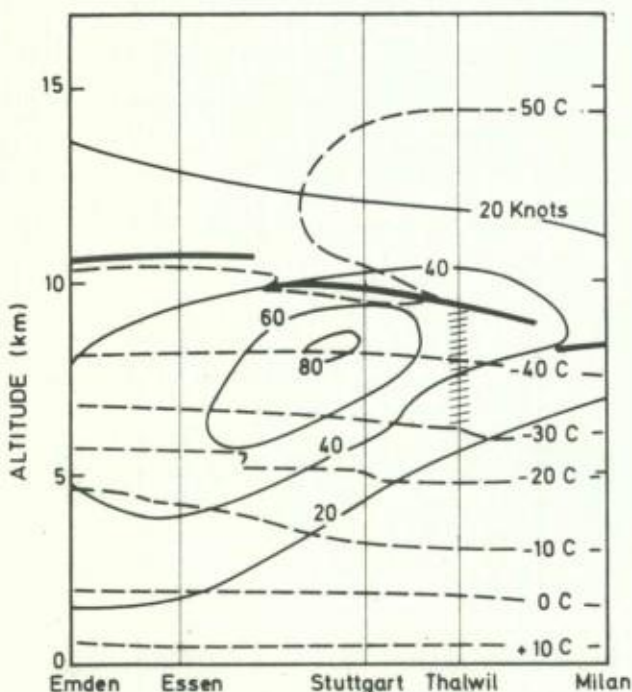

Fig. 26. Vertical profile from Emden (53°4N, 07°2E) to Thalwil (47°3N, 08°5E) and Milan (45°4N, 09°3E), June 12, 1967, at 1200 UT, from *Piaget* [1969, 1971]. Isothermal lines are in °C, isoplethic lines of the wind speed in knots (1 knot = 0.515 m s⁻¹), heavy lines denote the tropopause levels. Regions of ozone increase at Thalwil are indicated by shading.
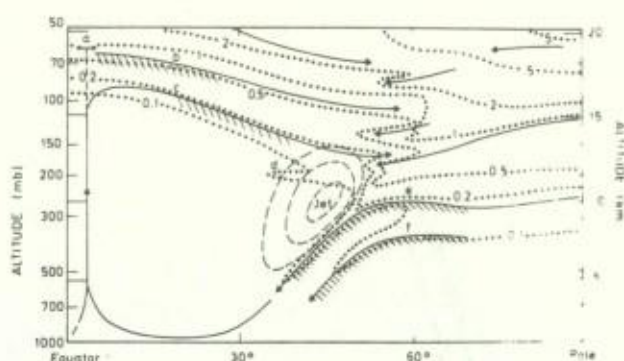

Fig. 27. Schematic meridian profile of exchanges between the stratosphere and troposphere, according to *Piaget* [1971]. Isentropic trajectories are represented by continuous lines, ozone mixing ratios (μg/g) by dotted lines, isopleths of wind speed in knots (1 knot = 0.515 m s⁻¹) by dashed lines, and conventional tropopauses by shading. The curves *a–f* are described in the text.

Finally, it is always useful to keep in mind that the differences, which occur with latitude and season, are due to an increase of the ozone concentrations below its peak An illustration of the latitudinal variation is given in Figure 31. where there is an indication of values between 0.25 cm and 0.45 cm from tropical region to high latitudes, respectively; such an increase is associated with a decrease of the tropopause height.

PHOTODISSOCIATION IN THE TROPOSPHERE AND STRATOSPHERE AND ITS EFFECTS

The photodissociation in the lower regions of the terrestrial atmosphere is of particular interest, since it is the necessary process to start various chemical reactions. Molecular oxygen is subject to dissociation above the ozone peak (~25 km) while ozone is photodissociated at ground level. The ozone photolysis (see for example, *Welge* [1974] for a recent analysis of the photolysis of O_x, HO_x, CO_x, and SO_x compounds) occurs in the visible region in the spectral range of the Chappuis bands with production of oxygen molecules and atoms in their normal states. The photodissociation coefficient is of the order of
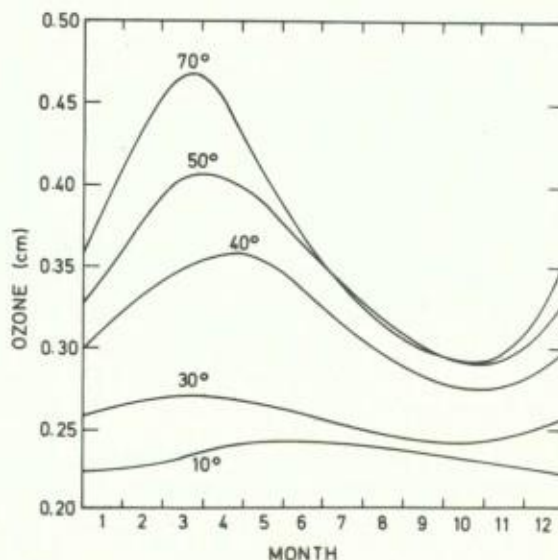

Fig. 28. Smoothed annual variation of the total amount of ozone at 10°, 30°, 40°, 50°, and 60° of north latitude, according to *Dobson* [1963]. Ozone amount in centimeters (STP).
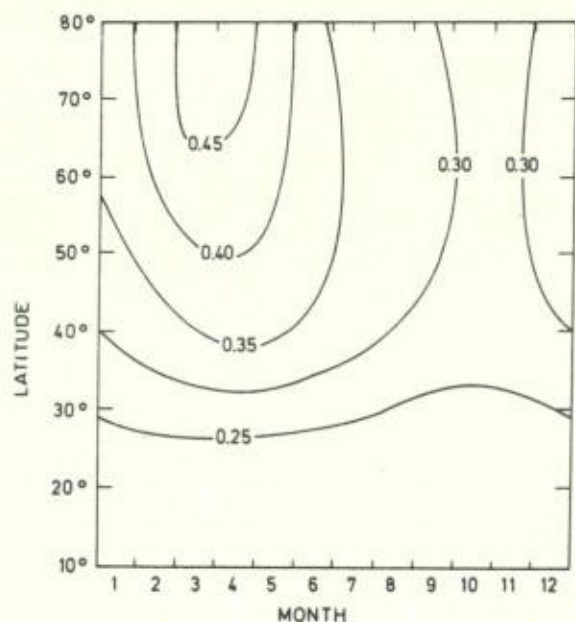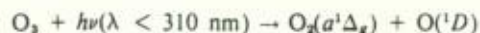
Fig. 29. Annual distributions of the total amount of ozone (cm STP) versus latitude, according to *Dobson* [1963].

$$J_3(\text{Chappuis}) = 3 \times 10^{-4} \text{ s}^{-1}$$

even at ground level.

In the ultraviolet, the important process is the photodissociation

$$O_3 + h\nu(\lambda < 310 \text{ nm}) \rightarrow O_2(a^1\Delta_g) + O(^1D)$$

The relative quantum yield near the threshold at 310 nm depends on the temperature. It has been measured by *Lin and DeMore* [1973a] at stratospheric temperature (233 K), and its variation with temperature at 313 nm has been observed by *Kuis et al.* [1975]. A graph illustrative of these results (Figure 32) shows that the quantum yield Φ to be used in the lower stratosphere may be taken as follows: $\Phi = 1.0$ at 300 ± 2.5 nm, 0.9 at 305 ± 2.5 nm, 0.3 at 310 ± 2.5 nm, and 0.05 at 315 ± 2.5 nm.

The production of $O(^1D)$ atoms, which react with H_2O and CH_4 and H_2 and N_2O and result in OH radicals and NO molecules, respectively, depends on the absolute ozone concentration and its vertical distribution. An example of the

Fig. 31. Examples of vertical distribution of ozone concentrations associated with an increase of the total amount related to latitude in the lower stratosphere.

vertical distribution of the $O(^1D)$ concentration is given in Figure 33 for July and January at 45°N. There is an increase from less than 1 $O(^1D)$ atom cm^{-3} below 20 km up to more than 100 cm^{-3} below the stratopause. Average values are indicated corresponding to a total of 13 hours in July and 11 hours in January. Thus the chemical action of $O(^1D)$ will depend on latitude and season, as well as on the effect of the ozone amount and its variations.

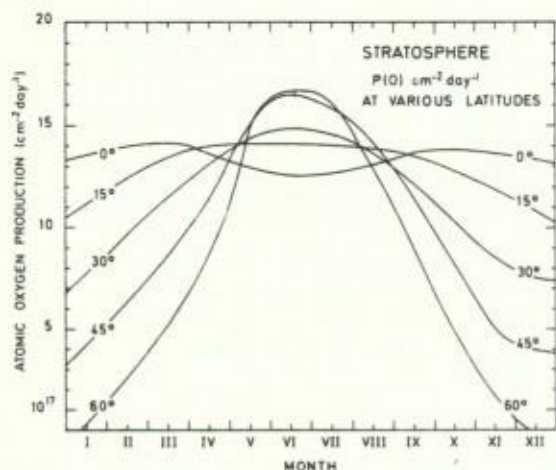The photodissociation processes of water vapor and methane are due mainly to the effect of Lyman α in the

Fig. 30. Annual distribution of atomic oxygen production (cm^{-2} day^{-1}) at 0°, 15°, 30°, 45°, and 60°N.

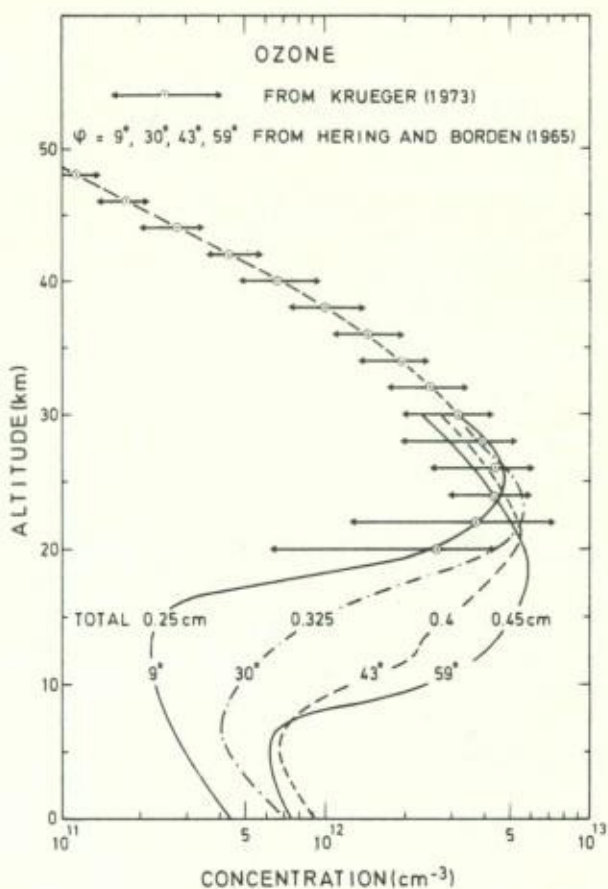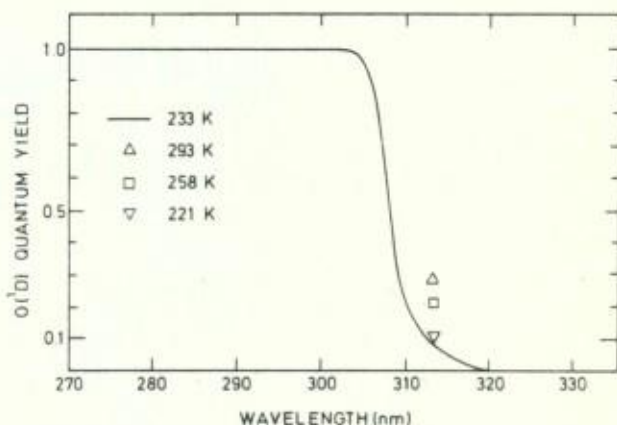Fig. 32. Quantum yield of $O(^1D)$ production versus wavelength. Curve at 233 K by *Lin and DeMore* [1973a], and at $\lambda = 313$ nm at 293, 258, and 251 K by *Kuis et al.* [1975].
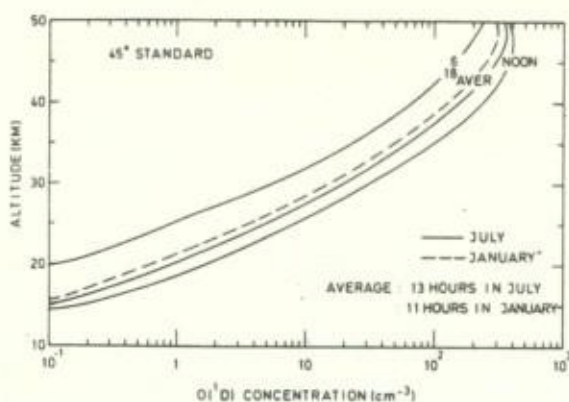
Fig. 33. Concentration of $O(^1D)$ atoms produced by ozone photolysis for standard conditions as given in Table 7.

Fig. 35. Examples of vertical distributions of direct photodissociation coefficients of hydrogen peroxide. Various solar zenith angles $\chi = 0°$, overhead sun conditions, to $\chi = 90°$, horizon [Nicolet, 1971].

mesosphere but also depend on the solar radiation absorbed in the spectral range of the Schumann-Runge bands, particularly in the lower mesosphere and upper stratosphere. Nevertheless, H_2O dissociation in the stratosphere is due mainly to the oxidation process by excited oxygen atoms $O(^1D)$. Photodissociation of H_2O must be considered only when it is required to determine the H_2 production at Lyman α, as an upper boundary condition. In the same way, CH_4 is subject to reactions with $O(^1D)$ and OH (see Figure 34) and its photodissociation, associated mainly with Lyman α and resulting in H_2 molecules, should be considered only when an upper boundary condition is needed or a knowledge of H_2 production is required. Figure 34 also illustrates CO_2 photodissociation, which plays a role in the upper stratosphere.

The absorption cross sections of HO_2 measured by *Hochanadel et al.* [1972] and *Pauckert and Johnston* [1972] at $\lambda < 260$ nm lead to the photodissociation of the hydroperoxyl radical in the stratosphere. This photodissociation can be neglected, since it is not as important as several other reactions playing significant roles.

The photodissociation of hydrogen peroxide, which must be introduced in the study of this stratospheric constituent, is based on laboratory measurements made in 1929 [*Urey et al.*, 1929] and in 1948 [*Holt et al.*, 1948] for two different spectral ranges. Using the published values of the absorption cross sections, the photodissociation coefficient obtained at the
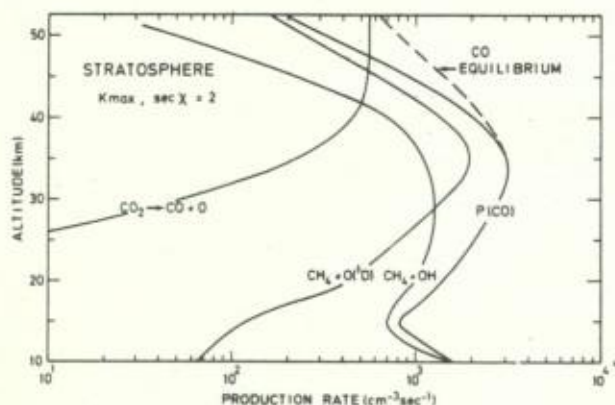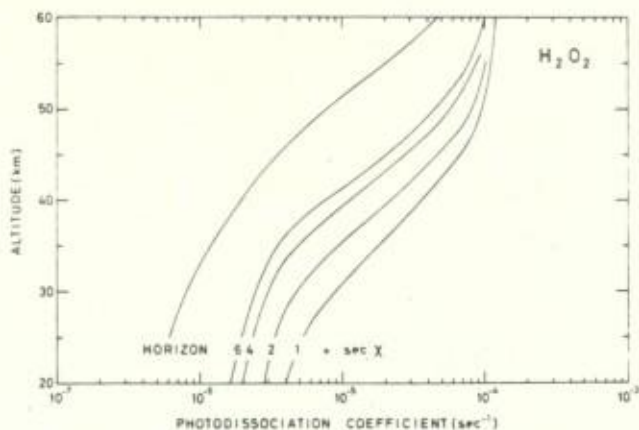
stratopause is about 10^{-4} s^{-1} (Figure 35) and reaches low values between 10^{-5} and 10^{-6} s^{-1} at 20 km. New laboratory data are needed in order to determine the loss processes of H_2O_2 in the stratosphere and also its exact aeronomic role. Finally, the vertical distribution of water vapor in the stratosphere is not affected by its own dissociation, since there is an immediate re-formation from hydroxyl and hydroperoxyl radicals. Its concentration depends on the exchange processes between the stratosphere and troposphere. However, the definitive decomposition of methane in the stratosphere leads to production of H_2 and OH or HO_2. There is therefore a continuous addition of water vapor molecules related to the transport of CH_4 from the troposphere to the stratosphere.

The photolysis of the oxides of nitrogen such as NO_2 and NO_3 depends strongly on radiation of $\lambda > 300$ nm, which leads to a high photodissociation coefficient, indication being that such molecules are always in photochemical equilibrium. Precise values are required for J_{NO_2}, since it determines the daytime ratio $n(NO_2)/n(NO)$. Various laboratory measurements of the absorption cross sections have been made at room temperature and seem to lead to $J_{NO_2} = 6 \pm 2 \times 10^{-3}$ s^{-1} at ground level [*Stedman et al.*, 1975a]. However, scattering effects [*Callis*, 1974] must be introduced into the determination of all photodissociation coefficients as a function of altitude. Detailed analyses by *Callis et al.* [1975] and by *Luther and Gelinas* [1975] show that the Rayleigh scattering and surface albedo alter the calculated photodissociation coefficients and can lead to significant modifications, particularly with variation of solar zenith angles.

The absorption spectrum of NO_3 has been analyzed in the visible region (450–680 nm) by *Johnston and Graham* [1974a], who find that the cross section is between 10^{-19} and 10^{-18} s^{-1}. If such an absorption leads to rapid photodissociations, NO_3 cannot play a leading role in the ozonosphere.

The behavior of nitrous and nitric acids is different, since their principal absorptions do not occur in the same spectral range [*Johnston and Graham*, 1974a]. The HNO_2 cross section between 300 and 400 nm varies between 10^{-20} and 10^{-19} cm^2, while the HNO_3 cross section [*Johnston and Graham*, 1973; *Biaumé*, 1973] increases from only about 10^{-22} cm^2 at 320 nm to 10^{-20} cm^2 at 280 nm in the Hartley continuum of ozone. HNO_2 is in photochemical equilibrium, while strong departures from photoequilibrium conditions must occur for HNO_3. A graph illustrative of the variation of the photodissociation
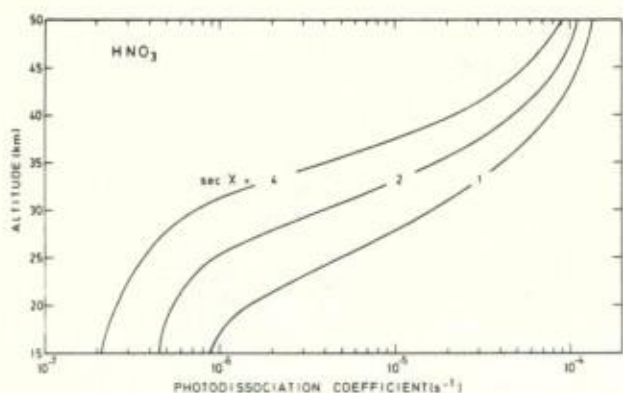

Fig. 34. Example of reactions destroying methane and producing carbon monoxide in the stratosphere. Solar zenith angle χ with sec $\chi = 2$ and arbitrary eddy diffusion coefficient K_{max} are used [*Nicolet and Peetermans*, 1973].

Fig. 36. Examples of vertical distribution of direct photodissociation coefficients of nitric acid for various solar zenith angles χ, sec χ = 1, 2, and 4 [*Biaumé*, 1973].

Fig. 37. Examples of vertical distribution of direct photodissociation coefficients of nitrous oxide for various solar zenith angles χ, sec χ = 1, 1.4, 2, and 4 [*Nicolet and Peetermans*, 1972].

coefficient with altitude (Figure 36) shows that J_{HNO_2} is not far from 10^{-4} s^{-1} at the stratopause but that its value decreases rapidly in the stratosphere and reaches less than 10^{-6} s^{-1} in the lower stratosphere. Its value is related to the ozone amount.

The absorption cross section of nitrous oxide varies within very low values less than 10^{-23} cm^2 between 310 and 250 nm, and its photodissociation coefficient (Figure 37) is not greater than 10^{-6} s^{-1} at the stratopause and reaches only values less than 10^{-9} s^{-1} in the low stratosphere. Its vertical distribution depends on its transport from the troposphere to the upper stratosphere, where its lifetime in the solar radiation field is only a few months. Its absolute concentration should be known with precision, particularly in the upper stratosphere, where the production of nitric oxide molecules depends on the reaction $O(^1D) + N_2O$.

The photodissociation of nitric oxide must be introduced into the upper stratosphere and mesosphere, since it plays a role in the determination of the upper boundary conditions of nitrogen oxides at the stratopause level. The NO dissociation depends strongly on the predissociation effect in the $\delta(0 - 0)$ and $\delta(1 - 0)$ bands near 191 and 183 nm, which are in the spectral range of the Schumann-Runge bands. An analysis made by *Cieslik and Nicolet* [1973] shows that the total photodissociation rate leads to $J_{NO} = 2 \times 10^{-6}$ s^{-1} and 8×10^{-7} s^{-1} for overhead sun conditions and a sun altitude of 30°, respectively, at the stratopause level. At the mesopause level, the average value is $J_{NO} = 6 \times 10^{-6}$ s^{-1}. Such values indicate that an NO molecule is still subject to a photodissociation process in the upper stratosphere.

Finally, the photodissociation of chlorine species, except Cl$_2$ (equation (152)), depends on the vertical ozone distribution and the absolute values of its stratospheric concentration. The various references, which are given in the analysis of chlorine atom production, reactions (159) to (161), indicate that the photodissociation of chlorofluoromethanes, carbon tetrachloride, hydrogen chloride, and various chlorine oxides occur only in the stratosphere. The photodissociation rates are relatively small, and departures from photochemical equilibrium conditions are always the rule. Their possible action on the ozone stratospheric equilibrium will be related to the various transport conditions.

FINAL INTRODUCTORY REMARKS

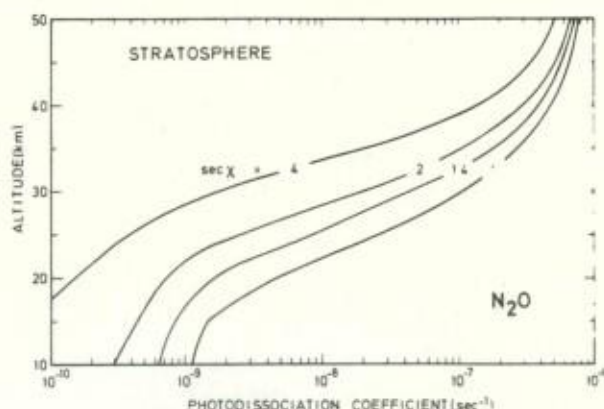We have seen that it is always possible to resolve the theoretical problem of stratospheric ozone with the introduc-

tion of correct aeronomic equations and with the adoption of the principal atmospheric parameters. However, it is not yet possible to determine with precision the behavior of certain minor constituents and also to follow the various aspects of the meteorological conditions. The boundary conditions, which are used in stratospheric models, are not always adopted to varying atmospheric conditions. On the other hand, the eddy diffusion coefficients, which are chosen for particular transport exchanges, are often ad hoc characteristics for vertical or vertical and latitudinal or vertical, latitudinal, and longitudinal features.

The cycle of carbon monoxide (Figure 38) is a prime example of problems which required special attention [*Robinson and Robbins*, 1971]. Without going into details [see, for example, *Seiler*, 1974; *Seiler and Schmidt*, 1974] it may be pointed out that the CO concentration must be known with precision in the lower stratosphere in order to determine the ratio $n(OH)/n(HO_2)$. Its stratospheric concentration should be known at each latitude and also when the tropopause level varies; an average value of the mixing ratio seems to be of the order of 5×10^{-8} in the lower stratosphere. The chemical aspects as considered by *Wofsy et al.* [1972], which are extremely important, must be analyzed with new observational data, since they are associated with the lower boundary conditions which must be applied to stratospheric CO.

In the same way, the tropospheric ozone problem requires more attention, since a photochemical theory has been proposed by *Chameides and Walker* [1973, 1974] and contested by *Fabian* [1974]. The essential problem is to determine the ac-
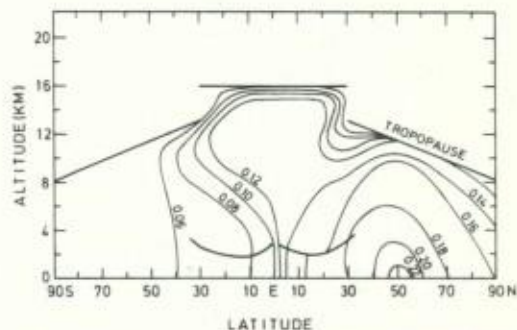

Fig. 38. Idealized cross section of the distribution of the CO mixing ratio in the troposphere over the Atlantic Ocean, according to *Seiler and Schmidt* [1974]. Mixing ratio in parts per million.
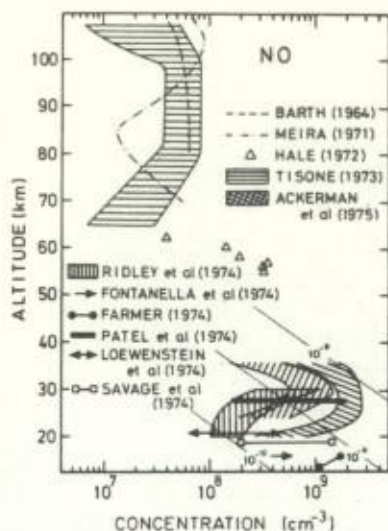
Fig. 39. Observed nitric oxide concentrations as collected by *Ackerman* [1975] indicating extremely variable mixing ratios in the stratosphere; all references are given by *Ackerman* [1975]; 10^{-10}, 10^{-9}, and 10^{-8} lines correspond to constant mixing ratios.

tion of the reaction between HO_2 and NO leading to OH and NO_2 when there is a source of OH or HO_2 radicals (CH_4, for example) with enough nitrogen oxides without direct production of oxygen atoms from O_2 photodissociation. Instead of (143), for daytime conditions, an equation such as

$$\frac{dn(O_3)}{dt} + n(O_3)[a_n n(OH) + a_{6e} n(HO_2) + b_4 n(NO)]$$

$$= n(NO_2) J_{NO_2} + P(N) \quad (206)$$

should be used as a first approximation.

The problem of the role of OH and HO_2 radicals as studied by *Warneck* [1974, 1975] in the troposphere must be kept in mind for the study of the lower stratosphere in the regions when the tropopause height varies with atmospheric conditions. At the present time, it is very difficult to determine the ratio $n(OH)/n(HO_2)$ and also the absolute values of their concentrations above the tropopause level.

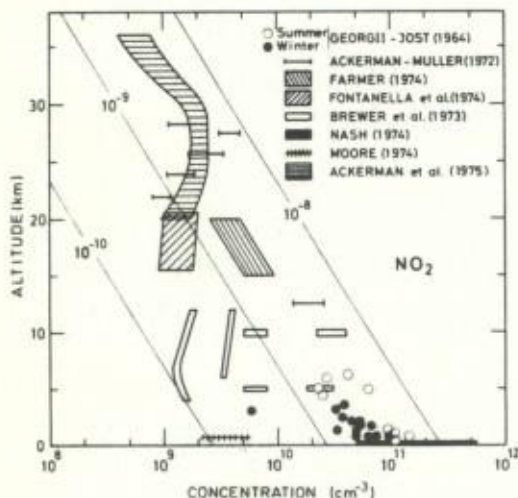Fig. 40. Observed nitrogen dioxide concentrations as collected by *Ackerman* [1975]; 10^{-10}, 10^{-9}, and 10^{-8} correspond to constant mixing ratios.
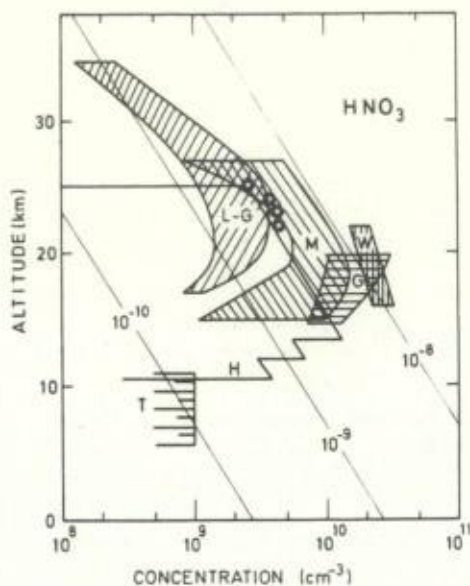

Fig. 41. Observed nitric acid concentrations as collected by *Ackerman* [1975]; 10^{-10}, 10^{-9}, and 10^{-8} lines correspond to constant mixing ratios; L-G denotes the measurements by *Lazrus and Gandrud* [1974]; M, *Murcray et al.* [1974]; G, *Fontanella et al.* [1974]; W, *Fried and Weinman* [1970]; and H, *Harries et al.* [1974]; T, analysis by the author.

The problems of H_2 and CH_4 are related in the stratosphere but may be considered as independent in the troposphere. Recent measurements by *Schmidt* [1974] and *Seiler and Schmidt* [1974] lead to an almost constant mixing ratio of 0.55 ppm for tropospheric molecular hydrogen which can be taken as the normal mixing ratio above the tropopause level. However, reaction of $O(^1D)$ with CH_4 and formaldehyde photodissociation in the stratosphere is a small source of H_2 molecules. Sampling [*Ehhalt*, 1974] in the stratosphere at various latitudes is required in order to obtain enough vertical profiles to compare with the calculated vertical distributions of methane and molecular hydrogen.

Methane plays an important role, since its average mixing ratio in the lower stratosphere of the order of 1.5×10^{-6} corresponds to an important fraction of the total amount of hydrogen atoms which can be available, since the H_2O mixing ratio [*Mastenbrook*, 1968, 1971] in the lower stratosphere is about $(3 \pm 1) \times 10^{-6}$. More stratospheric observations are needed since there are only two samplings [*Ehhalt et al.*, 1975] in the upper stratosphere. It is not yet clear how the vertical and horizontal transports play their role [*Wofsy et al.*, 1972; *Nicolet and Peetermans*, 1973] in the vertical and latitudinal vertical profiles of stratospheric CH_4. At the same time the atmospheric CH_4 cycle should be considered along with its various aspects involving the decomposing organic matter [*Robinson and Robbins*, 1971], the exact ^{14}C content [*Ehhalt*, 1967], and even special sources [*Deuser et al.*, 1973]. Since methane is subject to loss processes in the whole atmosphere with no re-formation process, its penetration into the stratosphere and mesosphere must be determined with great accuracy. At the present time, its residence time in the troposphere is not known with precision [*Junge*, 1974].

Nitrous oxide may be compared with methane, since they both have a natural origin and are both destroyed without any re-formation in the atmosphere. However, it seems that the loss process of N_2O molecules is due to a photodissociation process. The vertical distribution of its absolute concentration
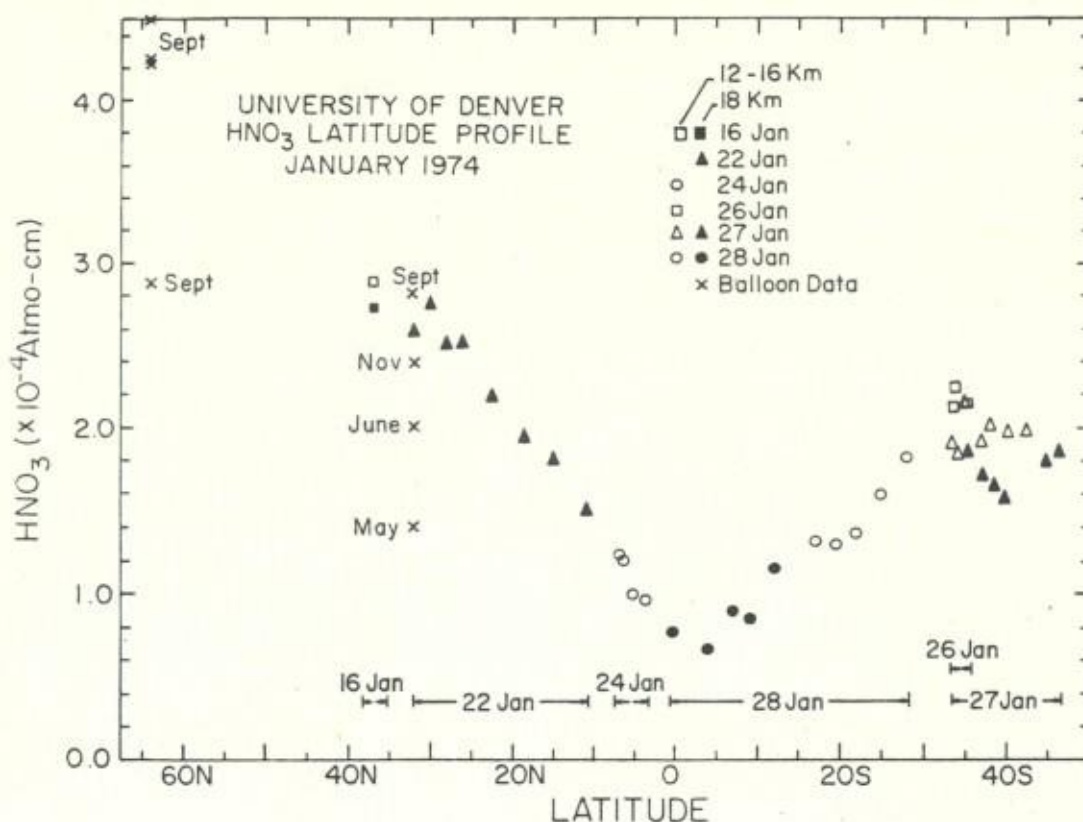
Fig. 42. Observed (January 1974) nitric acid amount as determined by the University of Denver; *Murcray et al.* [1975].

in the upper stratosphere should be known at various latitudes, since N_2O leads to NO when it reacts with $O(^1D)$. The detailed study by *Schütz et al.* [1970] shows that the average mixing ratio is 2.5×10^{-7} in the troposphere with perhaps an increase from 1966 to 1969 corresponding to the observation period. Since oceans and land act as sources of nitrous oxide [*Hahn*, 1974], a residence time of the order of 10 years [*Junge*, 1974] is short in comparison with the lifetime in the solar radiation field. Another loss process is required or the absorption cross sections of N_2O in the ultraviolet spectrum will not be correct. It is extremely important to develop an observational study of nitrous oxide, since it is directly related to the production of stratospheric nitric oxide.

Furthermore, the problem of the oxides of nitrogen and of the oxyacids of nitrogen is far from solution. The superabundance of sources of nitric oxide as described in the section on reactions in a nitrogen-hydrogen-oxygen atmosphere indicates that it is not yet possible to make quantitative statements without introducing ad hoc working hypotheses. We cannot here discuss the various observational and theoretical aspects. However, if we consider the first observational results as described by *Ackerman* [1975], we see (Figure 39) that the variation of the NO concentrations in the stratosphere requires an interpretation, since the nitrogen oxides are introduced in the stratospheric models. On the other hand, the observational results on the NO_2 concentrations in the stratosphere (and troposphere) as illustrated in Figure 40 are not yet sufficient to check the validity of theoretical results, particularly of the stratospheric models giving the vertical distribution of the ozone concentration. Observations at various latitudes are needed.

Finally, nitrous and nitric acids must remain the subject of careful observational analysis, since they are involved in the

nitric oxide cycle. Recent measurements at ground level of HNO_2 by *Nash* [1974] lead to mixing ratios from 1 to 10 ppb which must be explained by its various reactions with nitrogen oxides and hydroxyl and hydroperoxyl radicals. The stratospheric role of HNO_3 as a loss process of nitrogen oxides requires special attention. Recent measurements as shown in Figure 41 reveal the range of possible variations and particularly of the vertical distribution in the lower stratosphere. Very important observations have been made in 1974 by *Murcray et al.* [1975] on the HNO_3 total content at altitudes of 12–16 and 18 km. An example of their results is given in Figure 42 and clearly shows a strong latitude effect and also a seasonal effect. A variation of more than a factor of 3 must be taken into account in the analysis of the action of nitrogen oxides. There is therefore a clear indication that the introduction of observational data on stratospheric trace constituents in the analysis of stratospheric ozone will modify the present quantitative conclusions deduced from the theoretical models, which cannot consider all aspects related to aeronomic and meteorological processes.

REFERENCES

Ackerman, M., Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, edited by G. Fiocco, pp. 149–159, D. Reidel, Dordrecht, Netherlands, 1971.

Ackerman, M., Solar ultraviolet flux below 50 kilometers, *Can. J. Chem., 52*, 1505, 1974.

Ackerman, M., NO, NO$_2$ and HNO$_3$ below 35 km in the atmosphere, *J. Atmos. Sci., 32*, in press, 1975.

Ackerman, M., and C. Muller, Stratospheric nitrogen dioxide from infrared absorption spectra, *Nature, 240*, 300, 1972.

Ackerman, M., and P. Simon, Rocket measurement of solar fluxes at 1216 Å, 1450 Å and 1710 Å, *Solar Phys., 30*, 345, 1973.

Ackerman, M., F. Biaumé, and G. Kockarts, Absorption cross sections of the Schumann-Runge bands of molecular oxygen, *Planet. Space Sci., 18*, 1639, 1970.

Ackerman, M., J.-C. Fontanella, D. Frimout, A. Girard, N. Louisnard, and C. Muller, Simultaneous measurements of NO and NO$_2$ in the stratosphere, *Planet. Space Sci., 23*, 651, 1975.

Anderson, J. G., and F. Kaufman, Kinetics of the reaction OH(v = 0) + O$_3$ → HO$_2$ + O$_2$, *Chem. Phys. Lett., 19*, 483, 1973.

Anastasi, C., P. P. Bemand, and I. W. M. Smith, Rate constants for OH + NO$_2$ (+N$_2$) → HNO$_3$ (+N$_2$) between 358 and 220 K, *Chem. Phys. Lett.*, in press, 1975.

Anderson, J. G., J. J. Margitan, and F. Kaufman, Gas phase recombination of OH with NO and NO$_2$, *J. Chem. Phys., 60*, 3311, 1974.

Arvesen, J. C., R. N. Griffin, Jr., and B. D. Pearson, Jr., Determination of extraterrestrial solar spectral irradiance from a research aircraft, *Appl. Opt., 8*, 2215, 1969.

Barth, C. A., Rocket measurement of the nitric oxide dayglow, *J. Geophys. Res., 69*, 3301, 1964.

Basco, N., D. G. L. James, and F. C. James, A quantitative study of alkyl radical reactions by kinetic spectroscopy, 2, Combination of the methyl radical with the oxygen molecule, *Int. J. Chem. Kinet., 4*, 129, 1972.

Bates, D. R., Some reactions occurring in the earth's upper atmosphere, *Ann. Geophys., 8*, 194, 1952.

Bates, D. R., and P. B. Hays, Atmospheric nitrous oxide, *Planet. Space Sci., 15*, 189, 1967.

Bates, D. R., and M. Nicolet, Théorie de l'émission du spectre de la molécule OH dans le ciel nocturne, *C. R. Acad. Sci. Paris, 230*, 1943, 1950a.

Bates, D. R., and M. Nicolet, Atmospheric hydrogen, *Publ. Astron. Soc. Pacific, 62*, 106, 1950b.

Bates, D. R., and M. Nicolet, The photochemistry of water vapor, *J. Geophys. Res., 55*, 301, 1950c.

Bates, D. R., and A. E. Witherspoon, The photochemistry of some minor constituents of the earth's atmosphere (CO$_2$, CO, CH$_4$, N$_2$O), *Mon. Notic. Roy. Astron. Soc., 112*, 101, 1952.

Bauer, E., and F. R. Gilmore, Effect of atmospheric nuclear explosions on total ozone, *Rev. Geophys. Space Phys., 13*, 451, 1975.

Baulch, D. L., D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions*, vol. 1, *Homogeneous Gas Phase Reactions of the H$_2$-O$_2$ System*, 433 pp., Butterworths, London, 1972.

Baulch, D. L., D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions*, vol. 2, *Homogeneous Gas Phase Reactions of the H$_2$-N$_2$-O$_2$ System*, 557 pp., Butterworths, London, 1973.

Becker, K. H., W. Groth, and D. Kley, The rate constant of the aeronomic reaction N + O$_2$, *Z. Naturforsch. A, 24*, 1280, 1969.

Becker, K. H., W. Groth, and D. Thran, The mechanism of the air-afterglow NO + O → NO$_2$ + hν, *Chem. Phys. Lett., 15*, 215, 1972.

Bemand, P. P., M. A. A. Clyne, and R. T. Watson, Reactions of chlorine oxide radicals, 4, Rate constants for the reactions Cl + OClO, O + OClO, H + OClO, NO + OClO and O + ClO, *J. Chem. Soc., Faraday Trans. 1, 69*, 1356, 1973.

Bemand, P. P., M. A. A. Clyne, and R. T. Watson, Atomic resonance fluorescence and mass spectrometry for measurements of the rate constants for elementary reactions: O^3P_J + NO$_2$ → NO + O$_2$ and NO + O$_3$ → NO$_2$ + O$_2$, *J. Chem. Soc., Faraday Trans. 2, 70*, 564, 1974.

Biaumé, F., Nitric acid vapour absorption cross-section spectrum and its photodissociation in the stratosphere, *J. Photochem., 2*, 139, 1973.

Boland, B. C., B. B. Jones, R. Wilson, S. F. T. Engstrom, and G. Noci, A high resolution solar ultraviolet spectrum between 200 and 220 nm, *Phil. Trans. Roy. Soc. London, Ser. A, 270*, 29, 1971.

Brasseur, G., and M. Nicolet, Chemospheric processes of nitric oxide in the mesosphere and stratosphere, *Planet. Space Sci., 21*, 939, 1973.

Breen, J. E., and G. P. Glass, Rates of some hydroxyl radical reactions, *J. Chem. Phys., 52*, 1082, 1970.

Brewer, A. W., and J. R. Milford, The Oxford-Kew sonde, *Proc. Roy. Soc. London, Ser. A, 256*, 470, 1960.

Brewer, A. W., C. T. McElroy, and J. B. Kerr, Nitrogen dioxide concentrations in the atmosphere, *Nature, 246*, 129, 1973.

Broadfoot, A. L., The solar spectrum 2100–2300 Å, *Astrophys. J., 173*, 681, 1972.

Brown, R. D. H., and I. W. M. Smith, Absolute rate constants for the reactions of O(^3P) atoms with HCl and HBr, *Int. J. Chem. Kinet., 7*, 301, 1975.

Brueckner, G. E., and O. K. Moe, High angular resolution absolute intensity of the solar continuum from 1400 Å to 1790 Å, *Space Res., 12*, 1595, 1972.

Cadle, R. D., Daytime atmospheric O(^1D), *Disc. Faraday Soc., 37*, 66, 1964.

Callis, L. B., The importance of Rayleigh scattering on photochemical processes in the stratosphere (abstract), *Eos Trans. AGU, 56*, 1124, 1974.

Callis, L. B., V. Ramanathan, R. E. Boughner, and B. R. Barkstrom, The stratosphere: Scattering effects, a coupled 1-D model, and thermal balance effects, paper presented at the Fourth CIAP Conference, U.S. Dep. of Transp., Cambridge, Mass., 1975.

Calvert, J. C., J. A. Kerr, K. L. Demerjian, and R. D. McQuigg, Photolysis of formaldehyde as a hydrogen atom source in the lower atmosphere, *Science, 175*, 751, 1972.

Campbell, I. M., and C. N. Gray, Rate constants for O(^3P) recombination and association with N(^4S), *Chem. Phys. Lett., 18*, 607, 1973.

Carver, J. H., B. H. Horton, G. W. A. Lockey, and B. Rofe, Ultraviolet ion chamber measurements of the solar minimum brightness temperature, *Solar Phys., 27*, 347, 1972.

Cashion, J. K., and J. C. Polanyi, Infrared chemiluminescence for gaseous reactions atomic H plus O$_3$, *J. Chem. Phys., 30*, 316, 1959.

Chalonge, D., and F. W. P. Götz, Mesures diurnes et nocturnes de la quantité d'ozone contenue dans la haute atmosphère, *C. R. Acad. Sci. Paris, 189*, 704, 1929.

Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res., 78*, 8751, 1973.

Chameides, W., and J. C. G. Walker, Reply, *J. Geophys. Res., 79*, 4126, 1974.

Chapman, S., A theory of upper atmospheric ozone, *Mem. Roy. Meteorol. Soc., 3*, 103, 1930.

Chapman, S., The photochemistry of atmospheric oxygen, *Rep. Progr. Phys., 9*, 92, 1943.

Chapman, C. J., and R. P. Wayne, The reaction of atomic nitrogen and hydrogen with nitric acid, *Int. J. Chem. Kinet., 6*, 617, 1974.

Chappuis, J., Sur le spectre d'absorption de l'ozone, *C. R. Acad. Sci. Paris, 91*, 985, 1880.

Chappuis, J., Sur les spectres d'absorption de l'ozone et de l'acide pernitrique, *J. Phys. Paris, Ser. 2, 1*, 494, 1882.

Cicerone, R. J., R. S. Stolarski, and S. Walters, Stratospheric ozone destruction by man-made chlorofluoromethanes, *Science, 185*, 1165, 1974.

Cicerone, R. J., D. H. Stedman, and R. S. Stolarski, Estimate of late 1974 stratospheric concentration of gaseous chlorine compounds (ClX), *Geophys. Res. Lett., 2*, 219, 1975a.

Cicerone, R. J., S. Walters, and R. S. Stolarski, Chlorine compounds and stratospheric ozone, *Science, 188*, 375, 1975b.

Cieslik, S., and M. Nicolet, The aeronomic dissociation of nitric oxide, *Planet. Space Sci., 21*, 925, 1973.

Clyne, M. A. A., and J. A. Coxon, Kinetic studies of oxy-halogen radical systems, *Proc. Roy. Soc. London, Sec. A, 303*, 207, 1968.

Clyne, M. A. A., and S. Down, Kinetic behavior of OH $X^2\Pi$ and $A^2\Sigma^+$ using molecular resonance fluorescence spectroscopy, *J. Chem. Soc., Faraday Trans. 2, 70*, 253, 1974.

Clyne, M. A. A., and I. S. McDermid, Mass spectrometric determination of the rate of elementary reactions of NO and NO$_2$ with ground state N ^4S atoms, *J. Chem. Soc., Faraday Trans. 1, 71*, in press, 1975.

Clyne, M. A. A., and B. A. Thrush, Isotopic investigation of the reaction of oxygen atoms with nitrogen oxide, *Trans. Faraday Soc., 58*, 511, 1962.

Clyne, M. A. A., and B. A. Thrush, Rates of elementary processes in the chain reaction between hydrogen and oxygen, 1, Reaction of oxygen atoms, *Proc. Roy. Soc. London, Sec. A, 275*, 544, 1963.

Clyne, M. A. A., and R. F. Walker, Absolute rate constant for elementary reactions in the chlorination of CH_4, CD_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, $CDCl_3$ and $CBrCl_3$, J. Chem. Soc. Faraday Trans. 1, 69, 1547, 1973.

Clyne, M. A. A., and R. T. Watson, Kinetic studies of diatomic free radicals using mass spectrometry, 2, Rapid bimolecular reactions involving ClO $X^2\Pi$ radical, J. Chem. Soc., Faraday Trans. 1, 70, 2250, 1974.

Clyne, M. A. A., B. A. Thrush, and R. P. Wayne, Kinetics of the chemiluminescent reaction between nitric oxide and ozone, Trans. Faraday Soc., 60, 359, 1964.

Cornu, A., Sur la limite ultra-violette du spectre solaire, C. R. Acad. Sci. Paris, 88, 1101, 1879.

Cox, R. A., The photolysis of gaseous nitric acid, J. Photochem., 3, 175, 1974a.

Cox, R. A., The photolysis of nitrous acid in the presence of carbon monoxide and sulphur dioxide, J. Photochem., 3, 291, 1974b.

Cox, R. A., and R. G. Derwent, Kinetics of the reaction of HO_2 with nitric oxide and nitrogen dioxide, J. Photochem., 4, 139, 1975.

Craig, R. A., The observations and photochemistry of atmospheric ozone and their meteorological significance, Meteorol. Monogr., 1(2), 1–50, 1950.

Crutzen, P. J., Determination of parameters appearing in the 'dry' and the 'wet' photochemical theories for ozone in the stratosphere, Tellus, 21, 368, 1969.

Crutzen, P. J., The influence of nitrogen oxides on the atmospheric ozone content, Quart. J. Roy. Meteorol. Soc., 96, 320, 1970.

Crutzen, P. J., Ozone production rates in oxygen-hydrogen-nitrogen oxide atmosphere, J. Geophys. Res., 76, 7311, 1971.

Crutzen, P. J., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, Pure Appl. Geophys., 106–108, 1385, 1973.

Crutzen, P. J., A review of upper atmospheric chemistry, Can. J. Chem., 52, 1569, 1974a.

Crutzen, P. J., Estimates of possible future ozone reductions from continued use of fluoro-chloro-methanes (CF_2Cl_2, $CFCl_3$), Geophys. Res. Lett., 1, 205, 1974b.

Crutzen, P. J., I. S. A. Isaksen, and G. R. Reid, Solar proton events: Stratospheric sources of nitric oxides, Science, 189, 457, 1975.

Cvetanovic, R. J., Excited state chemistry in the stratosphere, Can. J. Chem., 52, 1452, 1974.

Davis, D. D., A kinetic review of atmospheric reactions involving H_xC_y compounds, Can. J. Chem., 52, 1405, 1974.

Davis, D. D., W. Braun, and A. M. Bass, Reactions of Cl $^2P_{3/2}$: Absolute rate constants for reaction with H_2, CH_4, C_2H_6, CH_2Cl_2, C_3Cl_4 and $c-C_6H_{12}$, Int. J. Chem. Kinet., 2, 101, 1970.

Davis, D. D., S. Fisher, and R. Schiff, Flash photolysis-resonance fluorescence kinetics study: Temperature dependence of the reaction $OH + CO \rightarrow CO_2 + H$ and $OH + CH_4 \rightarrow H_2O + CH_3$, J. Chem. Phys., 61, 2213, 1973a.

Davis, D. D., J. T. Herron, and R. H. Huie, Absolute rate constants for the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$ over the temperature range 230–339°K, J. Chem. Phys., 58, 530, 1973b.

Davis, D. D., W. A. Payne, and L. J. Stief, The hydroxyl radical in atmospheric chemical dynamics: Reaction with carbon monoxide, Science, 179, 280, 1973c.

Davis, D. D., W. Wong, and J. Lephardt, A laser flash photolysis-resonance fluorescence kinetic study: Reaction of $O(^3P)$ with O_3, Chem. Phys. Lett., 22, 273, 1973d.

Davis, D. D., J. Prusazcyk, M. Dwyer, and P. Kim, A stop-flow time-of-flight mass spectrometry kinetic study: Reaction of ozone with nitrogen dioxide and sulfur dioxide, J. Chem. Phys., 78, 1775, 1974a.

Davis, D. D., W. Wong, and R. Schiff, A dye laser flash photolysis kinetic study of the reaction of ground-state atomic oxygen with hydrogen peroxide, J. Phys. Chem., 78, 463, 1974b.

Davis, D. D., J. F. Schmidt, C. M. Neeley, and R. J. Hanrahan, Effect of wavelength in the gas-phase photolysis of carbon tetrachloride at 253.7, 184.9, 147.0, and 106.7 nm, J. Phys. Chem., 79, 11, 1975.

de la Rive, M., Letter to Arago, C. R. Acad. Sci. Paris, 20, 1287, 1845.

DeLuisi, J. J., Measurements of the extraterrestrial solar radiant flux from 2981 to 4000 Å and its transmission through the earth's atmosphere as it is affected by dust and ozone, J. Geophys. Res., 80, 345, 1975.

DeMore, W. B., Rate constants for the reactions of hydroxyl and hydroperoxyl radicals with ozone, Science, 180, 735, 1973.

DeMore, W. B., and E. Tschuikow-Roux, Temperature dependence of the reaction of OH and HO_2 with O_3, J. Phys. Chem., 78, 1447, 1974.

Detwiler, C. R., D. L. Garrett, J. D. Purcell, and R. Tousey, The intensity distribution in the ultraviolet solar spectrum, Ann. Geophys., 17, 263, 1961.

Deuser, W. G., E. T. Degens, and G. R. Harvey, Methane in Lake Kivu: New data bearing on its origin, Science, 181, 51, 1973.

Dobson, G. M. B., Observations of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, Proc. Roy. Soc. London, Ser. A, 129, 411, 1930.

Dobson, G. M. B., Exploring the Atmosphere, Clarendon Press, Oxford, 1963.

Dobson, G. M. B., Forty years' research on atmospheric ozone at Oxford: A history, Appl. Opt., 7, 387, 1968.

Dobson, G. M. B., The laminated structure of the ozone in the atmosphere, Quart. J. Roy. Meteorol. Soc., 99, 599, 1973a.

Dobson, G. M. B., Atmospheric ozone and the movement of the air in the stratosphere, Pure Appl. Geophys., 106–108, 1520, 1973b.

Dobson, G. M. B., and D. N. Harrison, Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, Proc. Roy. Soc. London, Ser. A, 110, 660, 1926.

Dobson, G. M. B., and D. N. Harrison, Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, Proc. Roy. Soc. London, Ser. A, 114, 521, 1927.

Dobson, G. M. B., D. N. Harrison, and J. Lawrence, Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, Proc. Roy. Soc. London, Ser. A, 122, 456, 1929.

Donnelly, R. F., and J. H. Pope, The 1-3000 Å solar flux for a moderate level of solar activity for use in modeling the ionosphere and upper atmosphere, Tech. Rep. ERL 276-SEL 25, Nat. Oceanic and Atmos. Admin., Boulder, Colo., August 1973.

Doucet, J., P. Sauvageau, and C. Sandorfy, Vacuum ultraviolet and photoelectron spectra of fluoro-chloro derivatives of methane, J. Chem. Phys., 58, 3708, 1973.

Downie, C. S., Stratospheric pollution: Aircraft engine emissions in the region above the tropopause as a function of aircraft altitude and tropopause height, paper presented at the Second International Conference on the Environmental Impact of Aerospace Operations on the High Atmosphere, Amer. Meteorol. Soc., Boston, Mass., July 1974.

Durie, R. A., and R. A. Ramsay, Absorption spectra of the halogen monoxides, Can. J. Phys., 36, 35, 1958.

Dütsch, H. U., Photochemische Theorie des atmosphärischen Ozons unter Berücksichtigung von Nichtgleichgewichtszuständen und Luftbewegungen, doctoral dissertation, Univ. of Zurich, Zurich, 1946.

Dütsch, H. U., The photochemistry of stratospheric ozone, Quart. J. Roy. Meteorol. Soc., 94, 483, 1968.

Dütsch, H. U., Atmospheric ozone and ultraviolet radiation, in Climate of the Free Atmosphere of World Survey of Climatology, vol. 4, edited by H. E. Landsberg, pp. 383–432, Elsevier, Amsterdam, Netherlands, 1969.

Dütsch, H. U., Photochemistry of atmospheric ozone, Advan. Geophys., 15, 219, 1971.

Dütsch, H. U., Recent developments in photochemistry of atmospheric ozone, Pure Appl. Geophys., 106–108, 1361, 1973.

Dütsch, H. U., Regular ozone soundings at the aerological station of the Swiss Meteorological Office at Payenne, Switzerland, 1968-1972, Rep. 10, Lab. Atmosphärenphys. ETH, Swiss Meteorol. Office, 1974.

Ehhalt, D. H., Methane in the atmosphere, J. Air Pollut. Contr. Ass., 17, 518, 1967.

Ehhalt, D. H., Sampling of stratospheric trace constituents, Can. J. Chem., 52, 1510, 1974.

Ehhalt, D. H., L. E. Heidt, R. H. Lueb, and E. A. Martell, Concentrations of CH_4, CO, CO_2, H_2, H_2O and N_2O in the upper stratosphere, J. Atmos. Sci., 32, 163, 1975.

Engleman, R., The vibrational state of hydroxyl radicals produced by flash photolysis of a water-ozone-argon mixture, J. Amer. Chem. Soc., 87, 4193, 1965.

Fabian, P., Comments on 'A photochemical theory of tropospheric ozone' by W. Chameides and J. C. G. Walker, J. Geophys. Res., 79, 4124, 1974.

Fabry, C., Rapport de la réunion de l'ozone et de l'absorption atmosphérique, Gerlands Beitr. Geophys., 24, 1, 1929.

Fabry, C., and H. Buisson, L'absorption de l'ultraviolet par l'ozone et la limite du spectre solaire, J. Phys. Paris, Ser. 5, 3, 196, 1913.

Fabry, C., and H. Buisson, Etude de l'extrémité ultraviolette du spectre solaire, J. Phys. Paris, Ser. 6, 2, 197, 1921a.

Fabry, C., and H. Buisson, A study of the ultra-violet end of the solar spectrum, *Astrophys. J.*, *54*, 297, 1921*b*.

Fabry, C., and H. Buisson, L'absorption des radiations dans la haute atmosphère. *Mem. Sci. Phys.*, *11*, 1–64, 1930.

Farmer, C. B., Infrared measurements of stratospheric composition. *Can. J. Chem.*, *52*, 1544, 1974.

Foley, H. M., and M. A. Ruderman, Stratospheric NO production from past nuclear explosions, *J. Geophys. Res.*, *78*, 4441, 1973.

Foner, S. N., and R. L. Hudson, Mass spectrometry of the HO₂ free radical, *J. Chem. Phys.*, *36*, 2681, 1962.

Fontanella, J.-C., A. Girard, L. Gramont, and N. Louisnard, Vertical distribution of NO, NO₂ and HNO₃, as derived from stratospheric absorption infrared spectra, Proceedings of the Third CIAP Conference, *DOT-TSC-OST-74-15*, p. 217, U.S. Dep. of Transp., Washington, D. C., 1974.

Fowler, A., and R. J. Strutt, Absorption bands of atmospheric ozone in the spectra of sun and stars, *Proc. Roy. Soc. London, Sec. A, 93*, 577, 1917.

Fried, P. M., and J. A. Weinman, Vertical distribution of HNO₃ vapor in the stratosphere, *Bull. Amer. Meteorol. Soc.*, *51*, 1006, 1970.

Friedman, H., S. W. Lichtman, and E. T. Byram, Photon counter measurements of solar X-rays and extreme ultraviolet light, *Phys. Rev.*, *83*, 1025, 1951.

Gaedtke, H., and J. Troe, Primary processes in the photolysis of NO₂, *Ber. Bunsenges. Phys. Chem.*, *79*, in press, 1975.

Garvin, D., and R. F. Hampson, Chemical kinetics data survey, 7, Tables of rate and photochemical data for modeling of the stratosphere (revised), *NBS IR-74-430*, Nat. Bur. of Stand., Washington, D. C., 1974.

Georgii, J.-W., and D. Jost, Untersuchung über die Verteilungen von Spurengasen in der freien Atmosphäre, *Pure Appl. Geophys.*, *59*, 217, 1964.

Glänzer, K., and J. Troe, Decomposition of nitric acid, *Ber. Bunsenges. Phys. Chem.*, *78*, 71, 1974.

Golde, M. F., A. E. Roche, and K. Kaufman, Absolute rate constant for the O + NO chemiluminescence in the near infrared, *J. Chem. Phys.*, *59*, 3953, 1973.

Goldsmith, P., A. F. Tuck, J. S. Fost, E. L. Simmons, and R. L. Newson, Nitrogen oxides, nuclear weapon testing, Concorde and stratospheric ozone, *Nature*, *244*, 545, 1973.

Goodeve, C. F., and F. D. Richardson, The absorption spectrum of chlorine trioxide and chlorine hexoxide, *Trans. Faraday Soc.*, *33*, 453, 1937.

Gorse, R. A., and D. H. Volman, Photochemistry of the gaseous hydrogen peroxide-carbon monoxide system: Rate constants for hydroxyl radical reactions with hydrogen peroxide and isobutane by competitive kinetics, *J. Photochem.*, *1*, 1, 1972.

Gorse, R. A., and D. H. Volman, Rate constants for hydroxyl radicals reactions with hydrocarbons and for hydrogen atom reactions with hydrogen peroxide, *J. Photochem.*, *3*, 115, 1974.

Götz, F. W. P., Das atmosphärische Ozon, *Ergeb. Kosmisch. Phys.*, *1*, 180–235, 1931.

Götz, F. W. P., Die verticale Verteilung des atmosphärischen Ozons, *Ergeb. Kosmisch. Phys.*, *3*, 253–325, 1938.

Götz, F. W. P., A. R. Meetham, and G. M. B. Dobson, The vertical distribution of ozone in the atmosphere, *Proc. Roy. Soc. London, Sec. A, 145*, 416, 1934.

Gray, D., E. Lissi, and J. Heicklen, The reaction of H₂O₂ with NO₂ and NO, *J. Phys. Chem.*, *76*, 1919, 1972.

Greenberg, R. I., and J. Heicklen, The reaction of O(¹D) with CH₄, *Int. J. Chem. Kinet.*, *4*, 417, 1972.

Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy, 3, Reactions with H₂O₂ in the range 300–458°K, *J. Phys. Chem.*, *72*, 406, 1968.

Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy, 5, Reactions with H₂ and CO in the range 300–500°K, *J. Chem. Phys.*, *51*, 5049, 1969.

Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy, 6, Reactions with alkanes in the range 300–500°K, *J. Chem. Phys.*, *53*, 1070, 1970.

Griggs, M., Atmospheric ozone, in *The Middle Ultraviolet: Its Science and Technology*, edited by A. E. S. Green, pp. 83–117, John Wiley, New York, 1966.

Hack, W., K. Hoyerman, and H. G. Wagner, The reaction NO + HO₂ → NO₂ + OH with OH + H₂O₂ → HO₂ + H₂O as a HO₂ source, *Int. J. Chem. Kinet.*, *7*, in press, 1975.

Hahn, J., The North Atlantic Ocean as a source of atmospheric N₂O, *Tellus*, *26*, 160, 1974.

Hale, L. C., and B. A. Pontano, Measurements of an immiscible constituent of the low ionosphere using a Lyman-alpha source and blunt probe, *Space Res.*, *10*, 208, 1972.

Hampson, J., Photochemical behavior of the ozone layer, *Tech. Note 1627*, Can. Arm. Res. and Dev. Establ., Quebec, Canada, 1964

Hampson, J., Chemiluminescent emissions observed in the stratosphere and mesosphere, in *Les Problèmes Météorologiques de la Stratosphère et de la Mésosphère*, edited by M. Nicolet, pp. 393–440, Presses Universitaries de France, Paris, 1966.

Hampson, J., Photochemical war on the atmosphere, *Nature*, *250*, 189, 1974.

Hampson, R. F., and D. Garvin, Chemical kinetic and photochemical data for modeling atmospheric chemistry, *NBS Tech. Note*, Nat. Bur. of Stand., Washington, D. C., 1975.

Harker, A. B., and H. S. Johnston, Photolysis of nitrogen dioxide to produce O, NO₂ and N₂O₅, *J. Phys. Chem.*, *77*, 1153, 1973.

Harries, J. E., D. G. Moss, and N. R. Swann, H₂O, O₃, N₂O and HNO₃ in the Arctic stratosphere, *Nature*, *250*, 475, 1974.

Hartley, W. N., On the absorption spectrum of ozone, *J. Chem. Soc.*, *39*, 57, 1881*a*.

Hartley, W. N., On the absorption of solar rays by atmospheric ozone. *J. Chem. Soc.*, *39*, 111, 1881*b*.

Heath, D. F., C. L. Mateer, and A. J. Krueger, The Nimbus-4 backscatter ultraviolet (BUV) atmospheric ozone experiment—Two years' operation, *Pure Appl. Geophys.*, *106–108*, 1238, 1973

Heidner, R. F., III, and D. Husain, Electronically excited oxygen atoms, O(2 ¹D₂): A time-resolved study of the collisional quenching by the gases H₂, D₂, NO, N₂O, NO₂, CH₄ and CH₃O₂ using atomic absorption spectroscopy in the vacuum ultraviolet, *Int. J. Chem. Kinet.*, *5*, 819, 1973.

Heidner, R. F., III, D. Husain, and J. R. Wiesenfeld, Kinetic investigation of electronically excited oxygen atoms, O(2¹D₂), by time-resolved attenuation of atomic resonance radiation in the vacuum ultraviolet, 2, Collisional quenching by the atmospheric gases N₂, O₂, CO, CO₂, H₂O and O₃, *J. Chem. Soc., Faraday Trans. 2, 69*, 927, 1973.

Hering, W. S., and T. R. Borden, Mean distributions of ozone density over North America, 1963–1964, *Environ. Res. Pap. 162*, Air Force Cambridge Res. Lab., Bedford, Mass., 1965.

Herron, J. T., and R. D. Penzhorn, Mass spectrometry study of the reaction of atomic oxygen with ethylene and formaldehyde, *J. Phys. Chem.*, *73*, 191, 1969.

Herzberg, G., The atmospheres of the planets, *J. Roy. Astron. Soc. Can.*, *45*, 100, 1951.

Hesstvedt, E., On the photochemistry of ozone in the ozone layer, *Geofys. Publ.*, *27*, 4, 1968.

Hinteregger, H. E., L. A. Hall, and G. Schmidtke, Solar XUV radiation and neutral particle distribution in July 1963 thermosphere, *Space Res.*, *5*, 1175, 1965.

Hippler, H., C. Schippert, and J. Troe, Photolysis of NO₂ and collisional energy transfer in the reaction O + NO → NO₂ and O + NO₂ → NO₃, *Int. J. Chem. Kinet.*, *7*, in press, 1975.

Hochanadel, C. J., J. A. Ghormley, and P. G. Ogren, Absorption spectrum and reaction kinetics of the HO₂ radical in the gas phase, *J. Chem. Phys.*, *56*, 4426, 1972.

Holt, R. K., C. R. McLane, and O. Oldenberg, Ultraviolet absorption spectrum of hydrogen peroxide, *J. Chem. Phys.*, *16*, 225, 638, 1948.

Houzeau, A., Preuve de la présence dans l'atmosphère d'un nouveau principe gazeux, l'oxygène naissant, *C. R. Acad. Sci. Paris*, *46*, 89, 1858.

Huggins, W., and Mrs. Huggins, On a new group of lines in the photographic spectrum of Sirius, *Proc. Roy. Soc. London*, *48*, 216, 1890.

Huie, R. E., and J. T. Herron, The rate constant for the reaction O₃ + NO → O₂ + NO₂ over the temperature range 259–362°K, *Chem. Phys. Lett.*, *27*, 411, 1974.

Huie, R. E., J. T. Herron, and D. D. Davis, Absolute rate constants for the reaction O + O₂ + M → O₃ + M in the temperature range 200–346°K, *J. Phys. Chem.*, *76*, 2653, 1972.

Hunt, B. G., Photochemistry of ozone in a moist atmosphere, *J. Geophys. Res.*, *71*, 1385, 1966.

Husain, D., L. J. Kirsch, and J. R. Wiesenfeld, Collisional quenching of electronically excited nitrogen atoms, N(2²D₂, 2²P₂) by time-resolved atomic absorption spectroscopy, *Faraday Disc. Chem. Soc.*, *53*, 201, 1972.

Jayanty, R. K. M., R. Simonaitis, and J. Heicklen, The photolysis of CCl₄ in the presence of O₂ or O₃ at 213.9 nm, and the reaction of O(¹D) with CCl₄, *J. Photochem.*, *4*, 203, 1975*a*.

Jayanty, R. K. M., R. Simonaitis, and J. Heicklen, The photolysis of chlorofluoromethanes in the presence of O_2 and O_3 at 213.9 nm and their reactions with $O(^1D)$, *J. Photochem.*, 4, in press, 1975b.

Johns, J. W. C., S. H. Priddle, and D. A. Ramsay, Electronic absorption spectra of HCO and DCO radicals, *Faraday Disc. Chem. Soc.*, 35, 90, 1963.

Johnston, H. S., Reduction of stratospheric ozone by nitrogen oxyde catalysts from supersonic transport exhaust, *Science*, 173, 517, 1971.

Johnston, H. S., Newly recognized vital nitrogen cycle, *Proc. Nat. Acad. Sci. U.S.*, 69, 2369, 1972.

Johnston, H. S., Photochemistry in the stratosphere—With applications to supersonic transports, *Acta Astronaut.*, 1, 135, 1974.

Johnston, H. S., and H. J. Crosby, Kinetics of the gas phase reaction between ozone and nitric oxide, *J. Chem. Phys.*, 22, 689, 1954.

Johnston, H. S., and R. A. Graham, Gas-phase ultraviolet spectrum of nitric acid vapor, *J. Phys. Chem.*, 77, 62, 1973.

Johnston, H. S., and R. A. Graham, Photochemistry of NO_2 and HNO_3 compounds, *Can. J. Chem.*, 52, 1415, 1974a.

Johnston, H. S., and R. A. Graham, Kinetics of the gas-phase reaction between ozone and nitrogen dioxide, *J. Chem. Phys.*, 60, 4628, 1974b.

Johnston, H. S., and G. Whitten, Instantaneous photochemical rates of the global stratosphere, *Pure Appl. Geophys.*, 106–108, 1468, 1973.

Johnston, H. S., E. D. Morris, Jr., and J. van den Bogaerde, Molecular modulation kinetic spectroscopy. ClOO and ClO_2 radicals in the photolysis of chlorine in oxygen, *J. Amer. Chem. Soc.*, 91, 7712, 1969.

Johnston, H. S., G. Whitten, and J. Birks, Effect of nuclear explosions on stratospheric nitric oxide and ozone, *J. Geophys. Res.*, 78, 6107, 1973.

Jordan, C., and A. Ridgeley, Solar limb and disk continuum intensities in the wavelength region 1450–1950 Å, *Mon. Notic. Roy. Astron. Soc.*, 168, 533, 1974.

Junge, C. E., Residence time and variability of tropospheric trace gases, *Tellus*, 26, 477, 1974.

Kaufman, F., Aeronomic reactions involving hydrogen, *Ann. Geophys.*, 20, 106, 1964.

Kaufman, F., Neutral reactions involving hydrogen and other minor constituents, *Can. J. Chem.*, 47, 1917, 1969.

Kaufman, F., Hydrogen chemistry: Perspective on experiment and theory, Atmospheres of Earth and Planets, edited by B. M. McCormac, D. Reidel, Dordrecht, Netherlands, in press, 1975.

Klemm, B. B., W. A. Payne, and L. J. Stief, Absolute rate parameters for the reaction of atomic hydrogen with H_2O_2, *Int. J. Chem. Kinet.*, 7, in press, 1975.

Krezenski, D. C., R. Simonaitis, and J. Heicklen, The reactions of $O(^3P)$ with ozone and carbonyl sulfite, *Int. J. Chem. Kinet.*, 3, 467, 1971.

Krueger, A. J., The mean ozone distribution from several series of rocket soundings to 52 km at latitudes from 58°S to 64°N, *Pure Appl. Geophys.*, 106–108, 1272, 1973.

Krueger, A. J., D. F. Heath, and C. L. Mateer, Variations in the stratospheric ozone field inferred from Nimbus satellite observations, *Pure Appl. Geophys.*, 106–108, 1254, 1973.

Kuis, S., R. Simonaitis, and J. Heicklen, Temperature dependence of the photolysis of ozone at 3130 Å, *J. Geophys. Res.*, 80, 1328, 1975.

Kulcke, W., and H. K. Paetzold, Über eine Radiosonde Bestimmung der verticale Ozonverteilung, *Ann. Meteorol.*, 8, 47, 1957.

Kurylo, M. J., Absolute rate constants for the reactions $H + O_2 + M \cdot HO_2 + M$ over the temperature range 203–404 K, *J. Phys. Chem.*, 76, 3518, 1972.

Labs, D., and H. Neckel, The solar constant, *Solar Phys.*, 19, 3, 1971.

Lazrus, A. L., and B. W. Gandrud, Distribution of stratospheric nitric acid vapor, *J. Atmos. Sci.*, 31, 1102, 1974.

Lazrus, A. L., B. Gandrud, R. Woodward, and W. Sedlacek, Stratospheric halogens: Measurements and in-situ determination of nitric acid measurements, paper presented at the Fourth CIAP Conference, U.S. Dep. of Transp., Washington, D. C., 1975.

Leovy, C. B., Atmospheric ozone: An analytic model for photochemistry in the presence of water vapor, *J. Geophys. Res.*, 74, 417, 1969.

Levy, H., II, Normal atmosphere: Large radicals and formaldehyde concentrations predicted, *Science*, 173, 141, 1971.

Levy, H., II, Photochemistry of the lower troposphere, *Planet. Space Sci.*, 20, 919, 1972.

Levy, H., II, Photochemistry of minor constituents in the troposphere, *Planet. Space Sci.*, 21, 575, 1973.

Lin, C-L., and W. B. DeMore, $O(^1D)$ production in O_3 photolysis near 3100 Å, *J. Photochem.*, 2, 161, 1973a.

Lin, C-L., and W. B. DeMore, Reactions of $O(^1D)$ with methane and ethane, *J. Phys. Chem.*, 77, 863, 1973b.

Lin, C-L., and F. Kaufman, Reactions of metastable nitrogen atom, *J. Chem. Phys.*, 55, 3760, 1971.

Lloyd, A. C., Evaluated and estimated kinetic data for phase reactions of the hydroperoxyl radical, *Int. J. Chem. Kinet.*, 6, 169, 1974.

Loewenstein, M., J. P. Paddock, I. G. Popoff, and H. F. Savage, NO and O_3 measurements in the lower stratosphere from a U-2 aircraft, *Nature*, 249, 817, 1974.

London, J., and S. Oltmans, Further studies of ozone and sunspots, *Pure Appl. Geophys.*, 106–108, 1302, 1973.

Lovelock, J. E., Atmospheric fluorine compounds as indicators of air movements, *Nature*, 230, 379, 1971.

Lovelock, J. E., Atmospheric turbidity and CCl_3F concentrations in rural Southern England and Southern Ireland, *Atmos. Environ.*, 6, 917, 1972.

Lovelock, J. E., Atmospheric halocarbons and stratospheric ozone, *Nature*, 252, 292, 1974.

Lovelock, J. E., Natural halocarbons in the air and in the sea, *Nature*, 256, 193, 1975.

Lovelock, J. E., R. J. Maggs, and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, *Nature*, 241, 194, 1973.

Luther, F. M., and R. G. Gelinas, Effect of molecular multiple scattering and surface albedo on atmospheric photodissociation rates, *J. Geophys. Res.*, 80, in press, 1975.

Mack, G. P. R., and B. A. Thrush, Reaction of oxygen atoms with carbonyl compounds, 1. Formaldehyde, *J. Chem Soc Faraday Trans 1*, 69, 208, 1973.

Makhover, Z. M., Height and temperature of the tropopause over the northern hemisphere (in Russian), *Meteorol. Gidrol.*, 7, 28, 1972.

Margitan, J. J., F. Kaufman, and J. G. Anderson, The reactions of OH with CH_4, *Geophys. Res. Lett.*, 1, 80, 1974.

Marsh, D., and J. Heicklen, Photolysis of fluorotrichloromethane, *J. Phys. Chem.*, 69, 4410, 1965.

Mastenbrook, H. J., Water vapor distribution in the stratosphere and high troposphere, *J. Atmos. Sci.*, 25, 299, 1968.

Mastenbrook, H. J., The variability of water vapor in the stratosphere, *J. Atmos. Sci.*, 28, 1495, 1971.

McCarthy, R. L., Fluorocarbons in the environment (abstract), *Eos Trans. AGU*, 56, 1153, 1974.

McConnell, J. C., Atmospheric ammonia, *J. Geophys. Res.*, 78, 7812, 1973.

McConnell, J. C., Uncertainties in stratospheric–mesospheric modeling, *Can. J. Chem.*, 52, 1625, 1974.

McConnell, J. C., and M. B. McElroy, Odd nitrogen in the atmosphere, *J. Atmos. Sci.*, 30, 1465, 1973.

McConnell, J. C., M. B. McElroy, and S. C. Wofsy, Natural sources of atmospheric CO, *Nature*, 233, 187, 1971.

McCrumb, J. L., and F. Kaufman, Kinetics of the $O + O_3$ reaction, *J. Chem. Phys.*, 57, 1270, 1972.

McElroy, M. B., and J. C. McConnell, Nitrous oxide: A natural source of stratospheric NO, *J. Atmos. Sci.*, 28, 1095, 1971.

McElroy, M. B., S. C. Wofsy, J. E. Penner, and J. C. McConnell, Atmospheric ozone: Possible impact of stratospheric aviation, *J. Atmos. Sci.*, 31, 287, 1974.

McGrath, W. D., and R. G. W. Norrish, Influence of water on the photolytic decomposition of ozone, *Nature*, 182, 235, 1958.

McQuigg, R. D., and J. G. Calvert, The photodecomposition of CH_2O, CD_2O, CHDO and CH_2O–CD_2O mixtures at xenon flash lamp intensities, *J. Amer. Chem. Soc.*, 91, 1950, 1969.

Mecke, R., The photochemical ozone equilibrium in the atmosphere, *Trans. Faraday Soc.*, 27, 375, 1931.

Meinel, A. B., OH emission bands in the spectrum of the night sky, *Astrophys. J.*, 111, 555, 1950.

Meira, L. G., Jr., Rocket measurements of upper atmospheric nitric oxide and their consequences to the lower ionosphere, *J. Geophys. Res.*, 76, 202, 1971.

Milstein, R., and F. S. Rowland, Quantum yield for the photolysis of CF_2Cl_2 in O_2, *J. Phys. Chem.*, 79, 669, 1975.

Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine atom-catalysed destruction of ozone, *Nature*, 249, 810, 1974a.

Molina, M. J., and F. S. Rowland, Predicted present stratospheric abundances of chlorine species from photodissociation of carbon tetrachloride, *Geophys. Res. Lett.*, 1, 309, 1974b.

Molina, M. J., and F. S. Rowland, Some unmeasured chlorine atom

reaction rates important for stratospheric modeling of chlorine atom catalyzed removal of ozone, *J. Phys. Chem.*, 79, 667, 1975.

Moore, H., Isotopic measurement of atmospheric nitrogen compounds, *Tellus*, 26, 169, 1974.

Morley, C., and I. W. M. Smith, Rate measurements of OH by resonance absorption, 1, Reactions of OH with NO_2 and NO, *J. Chem. Soc., Faraday Trans. 2*, 68, 1016, 1972.

Morris, E. D., Jr., and H. Niki, Mass spectrometric study of the reaction of hydroxyl radical with formaldehyde, *J. Chem. Phys.*, 55, 1991, 1971.

Morris, E. D., Jr., and H. Niki, Reaction of dinitrogen pentoxide with water, *J. Phys. Chem.*, 77, 1929, 1973.

Murcray, D. G., et al., Stratospheric mixing ratio profiles of several trace gases as determined from balloon-borne infrared spectrometers, paper presented at the IAMAP Conference, Melbourne, Australia, 1974.

Murcray, D. G., D. D. Barker, J. N. Brooks, A. Goldman, and W. J. Williams, Seasonal and latitudinal variation of the stratospheric concentration of HNO_3, *Geophys. Res. Lett.*, 2, 223, 1975.

Murray, A. J., and J. P. Riley, Occurrence of some chlorinated aliphatic hydrocarbons in the environment, *Nature*, 242, 37, 1973.

Myer, J. A., and J. A. R. Samson, Vacuum-ultraviolet absorption cross sections of CO, HCl and ICN between 1050 A and 2100 A, *J. Chem. Phys.*, 52, 266, 1970.

Nash, T., Nitrous acid in the atmosphere and laboratory experiments on its photolysis, *Tellus*, 26, 175, 1974.

Nicolet, M., Contribution à l'étude de la structure de l'ionosphère, *Mem. Inst. Roy. Meteorol. Belg.*, 19, 162, 1945.

Nicolet, M., The aeronomic problem of nitrogen oxides, *J. Atmos. Terr. Phys.*, 7, 152, 1955a.

Nicolet, M., Nitrogen oxides and the airglow, *J. Atmos. Terr. Phys.*, 7, 297, 1955b.

Nicolet, M., Nitrogen oxides in the chemosphere, *J. Geophys. Res.*, 70, 679, 1965a.

Nicolet, M., Ionospheric processes and nitric oxide, *J. Geophys. Res.*, 70, 691, 1965b.

Nicolet, M., Ozone and hydrogen reactions, *Ann. Geophys.*, 26, 531, 1970a.

Nicolet, M., The origin of nitric oxide in the terrestrial atmosphere, *Planet. Space Sci.*, 18, 1111, 1970b.

Nicolet, M., Aeronomic reactions of hydrogen and ozone, in *Mesospheric Models and Related Experiments*, edited by G. Fiocco, pp. 1–51, D. Reidel, Dordrecht, Netherlands, 1971.

Nicolet, M., Aeronomic chemistry of the stratosphere, *Planet. Space Sci.*, 20, 1671, 1972.

Nicolet, M., An overview of aeronomic processes in the stratosphere and mesosphere, *Can. J. Chem.*, 52, 1381, 1974.

Nicolet, M., On the production of nitric oxide by cosmic rays in the mesosphere and stratosphere, *Planet. Space Sci.*, 23, 637, 1975.

Nicolet, M., and P. Mange, The dissociation of oxygen in the high atmosphere, *J. Geophys. Res.*, 59, 15, 1954.

Nicolet, M., and W. Peetermans, The production of nitric oxide in the stratosphere by oxidation of nitrous oxide, *Ann. Geophys.*, 28, 751, 1972.

Nicolet, M., and W. Peetermans, On the vertical distribution of carbon monoxide and methane in the stratosphere, *Pure Appl. Geophys.*, 106–108, 1400, 1973.

Nicolet, M., and E. Vergison, L'oxyde azoteux dans la stratosphère, *Aeron. Acta, A-91*, 1971.

Niki, H., Reaction kinetics involving O and N compounds, *Can. J. Chem.*, 52, 1397, 1974.

Nishi, K., Observation of the absolute intensity and the centre-to-limb variation of the sun in the vacuum ultraviolet region, *Solar Phys.*, 33, 23, 1973.

Nishi, K., K. Higashi, A. Yamaguchi, and Z. Suemoto, Observation of the absolute intensity of the sun in the vacuum ultraviolet region, *Bull. Inst. Space Aeronaut. Sci., Univ. Tokyo*, 10, 611, 1974.

Norton, R. B., and C. A. Barth, Theory of nitric oxide in the earth's atmosphere, *J. Geophys. Res.*, 75, 3903, 1970.

Ogawa, M., Absorption cross sections of O_2 and CO_2 continua in the Schumann and far-uv regions, *J. Chem. Phys.*, 54, 2550, 1971.

Paetzold, H. K., The influence of solar activity on the stratospheric ozone layer, *Pure Appl. Geophys.*, 106–108, 1308, 1973.

Parkes, D. A., D. M. Paul, C. P. Quinn, and R. C. Robson, The ultraviolet absorption by alkyperoxy radicals and their mutual reactions, *Chem. Phys. Lett.*, 23, 425, 1973.

Parkinson, W. H., and E. M. Reeves, Measurements in the solar spectrum between 1400 and 1875 Å with a rocket-borne spectrometer, *Solar Phys.*, 10, 342, 1969.

Pate, C. T., B. J. Finlayson, and J. N. Pitts, Jr., A long path infrared spectroscopic study of the reaction of methylperoxy free radicals with nitric oxide, *J. Amer. Chem. Soc.*, 96, 6554, 1974.

Patel, C. K. N., E. G. Burkhardt, and C. A. Lambert, Spectroscopic measurements of stratospheric nitric oxide and water vapor, *Science*, 184, 1173, 1974.

Paukert, T. T., and H. S. Johnston, Spectra and kinetics of the hydroperoxyl free radical in the gas phase, *J. Chem. Phys.*, 56, 2824, 1972.

Payne, W. A., L. J. Stief, and D. D. Davis, A kinetics study of the reaction of HO_2 with SO_2 and NO, *J. Amer. Chem. Soc.*, 95, 7614, 1973.

Phillips, L. F., and H. I. Schiff, Reactions in the atomic nitrogen-ozone systems, *J. Chem. Phys.*, 36, 1509, 1962.

Piaget, A., Etude synoptique de cas particuliers de la distribution horizontale et verticale de l'ozone atmosphérique, *Ann. Geophys.*, 25, 183, 1969.

Piaget, A., Utilisation de l'ozone atmosphérique comme traceur des échanges entre la troposphère et la stratosphère, *Veröff. Schweiz. Meteorol. Zentralanstalt*, 21, 1–71, 1971.

Pitts, J. N., Jr., A. C. Lloyd, and J. L. Sprung, Chemical reactions in urban atmospheres and their application to air pollution control strategies, paper presented at the International Symposium on Environmental Measures, Geneva, Oct. 1973.

Pitts, J. N., Jr., H. L. Sandoval, and R. Atkinson, Relative rate constants for the reaction of $O(^1D)$ atoms with fluorocarbons and N_2O, *Chem. Phys. Lett.*, 29, 31, 1974.

Prabhakara, C., E. B. Rodgers, and V. V. Salomonson, Remote sensing of the global distribution of total ozone and the inferred upper-tropospheric circulation from Nimbus Iris experiments, *Pure Appl. Geophys.*, 106–108, 1226, 1973.

Regener, V. H., On a sensitive method for the recording of atmospheric ozone, *J. Geophys. Res.*, 65, 3975, 1960.

Ridley, B. A., J. A. Davenport, L. J. Stief, and K. H. Welge, Absolute rate constant for the reaction $H + H_2CO$, *J. Chem. Phys.*, 57, 520, 1972.

Ridley, B. A., H. I. Schiff, A. Shaw, and L. R. Megill, In-situ measurements of NO in the stratosphere using chemiluminescence, Proceedings of the Third CIAP Conference, *DOT-TSC-OST-74-15*, p. 193, U.S. Dep. of Transp., Washington, D. C., 1974.

Robinson, E., and R. C. Robbins, Emissions, concentrations, and fate of gaseous atmospheric pollutants, in *Air Pollution Control*, part 2, edited by W. Strauss, pp. 3–93, John Wiley, New York, 1971.

Romand, J., Absorption ultraviolette dans la région de Schumann; Etude de: HCl, BrH et IH gazeux, *Ann. Phys. Paris*, 4, 527, 1949.

Rottman, G. R., Disc values of the solar ultraviolet flux, 1150 to 1900 Å (abstract), *Eos Trans. AGU*, 56, 1157, 1974.

Rowland, F. S., and M. J. Molina, Chlorofluoromethanes in the environment, *Rev. Geophys. Space Phys.*, 13, 1, 1975.

Ruderman, M. A., and J. W. Chamberlain, Origin of the sunspot modulation of ozone: Its implications for stratospheric NO injection, *Planet. Space Sci.*, 23, 247, 1975.

Russell, B. R., L. O. Edwards, and J. W. Raymonda, Vacuum ultraviolet absorption spectra of the chloromethanes, *J. Amer. Chem. Soc.*, 95, 2129, 1973.

Ryan, J. A., and N. R. Mukherjee, Sources of stratospheric gaseous chlorine, *Rev. Geophys. Space Phys.*, 13, this issue, 1975.

Sandoval, H. L., R. Atkinson, and J. N. Pitts, Jr., Reactions of electronically excited $O(^1D)$ atoms with fluorocarbons, *J. Photochem.*, 3, 325, 1974.

Sanhueza, E., and J. Heicklen, Chlorine-atom sensitized oxidation of dichloromethane and chloromethane, *J. Phys. Chem.*, 79, 7, 1975.

Savage, H. E., M. Loewenstein, and R. C. Whitten, In-situ measurements of NO and O_3 in the lower stratosphere, paper presented at the Second International Conference on the Environmental Impact of Aerospace Operations on the Atmosphere, Amer. Meteorol. Soc., Boston, Mass., July 1974.

Schmidt, U., Molecular hydrogen in the atmosphere, *Tellus*, 26, 78, 1974.

Schönbein, C. F., Recherches sur la nature de l'odeur qui se manifeste dans certaines actions chimiques, *C. R. Acad. Sci. Paris*, 10, 706, 1840a.

Schönbein, C. F., Beobachtungen über den bei der Elektrolysation des Wassers und dem Ausströmen der gewöhnlichen Elektricität aus Spitzen sich entwikkelnden Geruch, *Ann. Phys. Chem.*, 50, 616, 1840b.

Schütz, K., C. Junge, R. Beck, and B. Albrecht, Studies of atmospheric N₂O, *J. Geophys. Res.*, *75*, 2230, 1970.

Seery, D. J., and D. Britton, The continuous absorption spectra of chlorine, bromine, bromine chloride, iodine chloride and iodine bromide, *J. Phys. Chem.*, *68*, 2263, 1964.

Seiler, W., The cycle of atmospheric CO, *Tellus*, *26*, 116, 1974.

Seiler, W., and U. Schmidt, New aspects on CO and H₂ cycles in the atmosphere, paper presented at the IAMAP Conference, Melbourne, Australia, 1974.

Sie, B. K. T., R. Simonaitis, and J. Heicklen, The reaction of OH with CO, *Int. J. Chem. Kinet.*, *7*, in press, 1975a.

Sie, B. K. T., R. Simonaitis, and J. Heicklen, The reaction of OH with NO, *Int. J. Chem. Kinet.*, *7*, in press, 1975b.

Simon, P., Problem measurements of solar fluxes between 1960 A and 2300 A, *Aeron. Acta A*, *123*, 1-14, 1974a.

Simon, P., Nouvelles mesures de l'ultraviolet solaire dans la stratosphère, *Aeron. Acta A*, *145*, 1-19, 1974b.

Simonaitis, R., and J. Heicklen, The mechanism of the H₂O-catalyzed chain decomposition of O₃ and the reaction of HO with O₃, *J. Photochem.*, *2*, 309, 1973a.

Simonaitis, R., and J. Heicklen, Reactions of HO₂ with carbon monoxide and nitric oxide and of O(¹D) with water, *J. Phys. Chem.*, *77*, 1096, 1973b.

Simonaitis, R., and J. Heicklen, Reaction of HO₂ with O₃, *J. Phys. Chem.*, *77*, 1932, 1973c.

Simonaitis, R., and J. Heicklen, Reaction of HO₂ with NO and NO₂, *J. Chem. Phys.*, *78*, 673, 1974a.

Simonaitis, R., and J. Heicklen, Reactions of CH₃O₂ with NO and NO₂, *J. Phys. Chem.*, *78*, 2417, 1974b.

Simonaitis, R., and J. Heicklen, Reactions of CH₃, CH₃O and CH₃O₂ radicals with O₃, *J. Phys. Chem.*, *79*, 298, 1975a.

Simonaitis, R., and J. Heicklen, Perchloric acid: A possible sink for stratospheric chlorine, *Planet. Space Sci.*, *23*, in press, 1975b.

Simonaitis, R., and J. Heicklen, The reaction of HO₂ with NO and NO₂ and of OH with NO, *J. Phys. Chem.*, *79*, in press, 1975c.

Simmonds, P. G., S. L. Kerrin, J. E. Lovelock, and F. H. Shair, Distribution of atmospheric halocarbons in the air over the Los Angeles basin, *Atmos. Environ.*, *8*, 209, 1974.

Slagle, I. R., F. J. Pruss, Jr., and D. Gutman, Kinetics into the steady state, 1, Study of the reaction of oxygen atoms with methyl radicals, *Int. J. Chem. Kinet.*, *6*, 111, 1974.

Slanger, T. G., B. J. Wood, and G. Black, Temperature coefficient for N(²D) quenching by O₂ and N₂O, *J. Geophys. Res.*, *76*, 8430, 1971.

Slanger, T. G., B. J. Wood, and G. Black, Investigation of the rate coefficient for O(³P) + NO₂ → O₂ + NO, *Int. J. Chem. Kinet.*, *5*, 615, 1973.

Smith, I. W. M., and R. Zellner, Rate measurement of reactions of OH by resonance absorption, 2, Reactions of OH with CO, C₂H₄ and C₂H₂, *J. Chem. Soc., Faraday Trans. 2*, *69*, 1617, 1973.

Smith, I. W. M., and R. Zellner, Rate measurements of reactions of OH by resonance absorption, 3, Reactions of OH with H₂, D₂ and hydrogen and deuterium halides, *J. Chem. Soc., Faraday Trans. 2*, *70*, 1045, 1974.

Smith, I. W. M., and R. Zellner, Rate measurements of reactions of OH by resonance absorption, 4, Reactions of OH with NH₃ and HNO₃, *Int. J. Chem. Kinet.*, *7*, in press, 1975.

Sperling, H. P., and S. Toby, The photochemical decomposition of gaseous formaldehyde, *Can. J. Chem.*, *51*, 471, 1973.

Spicer, C. W., A. Villa, H. A. Wiebe, and J. Heicklen, Reactions of methylperoxy radicals with nitric oxide and nitrogen dioxide, *J. Amer. Chem. Soc.*, *95*, 13, 1973.

Stedman, D. H., W. Chameides, and J. O. Jackson, Comparison of experimental and computed values for j(NO₂), *Geophys. Res. Lett.*, *2*, 22, 1975a.

Stedman, D. H., W. Chameides, and R. J. Cicerone, The vertical distribution of soluble gases in the troposphere, *Geophys. Res. Lett.*, *2*, 333, 1975b.

Stolarski, R. S., and R. J. Cicerone, Stratospheric chlorine: A possible sink for ozone, *Can. J. Chem.*, *52*, 1610, 1974.

Strobel, D. F., Diurnal variation of nitric oxide in the upper atmosphere, *J. Geophys. Res.*, *76*, 2441, 1971a.

Strobel, D. F., Odd nitrogen in the mesosphere, *J. Geophys. Res.*, *76*, 8384, 1971b.

Strobel, D. F., D. M. Hunten, and M. B. McElroy, Production and diffusion of nitric oxide, *J. Geophys. Res.*, *75*, 4307, 1970.

Su, C.-W., and E. D. Goldberg, Chlorofluorocarbons in the atmosphere, *Nature*, *245*, 27, 1973.

Thekaekara, M. P., Solar energy outside the earth's atmosphere, *Solar Energy*, *14*, 109, 1973.

Thekaekara, M. P., Extraterrestrial solar spectrum, 3000-6100 Å at 1 Å intervals, *Appl. Opt.*, *13*, 518, 1974.

Tisone, G. C., Measurements of NO densities during sunrise at Kauai, *J. Geophys. Res.*, *78*, 746, 1973.

Trainor, D. W., and C. W. von Rosenberg, Flash photolysis study of the gas phase recombination of hydroxyl radicals, *J. Chem. Phys.*, *61*, 1010, 1974a.

Trainor, D. W., and C. W. von Rosenberg, Energy partitioning in the reaction OH + CO → CO₂ + H, *Chem. Phys. Lett.*, *24*, 35, 1974b.

Tsang, W., Comparisons between experimental and calculated rate constants for dissocation and combinations involving small polyatomic molecules, *Int. J. Chem. Kinet.*, *5*, 947, 1973.

Urey, H. C., L. C. Dawsey, and F. O. Rise, The absorption spectrum and decomposition of hydrogen peroxide by light, *J. Amer. Chem. Soc.*, *51*, 1371, 1929.

Vassy, A., Radiosonde spéciale pour la mesure de la répartition verticale de l'ozone atmosphérique, *J. Sci. Meteorol.*, *10*, 63, 1958.

Warneck, P., Cosmic radiation as a source of odd nitrogen in the stratosphere, *J. Geophys. Res.*, *77*, 6589, 1972.

Warneck, P., On the role of OH and HO₂ radicals in the troposphere, *Tellus*, *26*, 39, 1974.

Warneck, P., OH production rates in the troposphere, *Planet. Space Sci.*, *23*, in press, 1975.

Washida, N., and K. Bayes, The rate of reactions of methyl radicals with atomic oxygen, *Chem. Phys. Lett.*, *23*, 373, 1973.

Washida, N., R. I. Martinez, and K. D. Bayes, The oxidation of formyl radical, *Z. Naturforsch. A*, *29*, 251, 1974.

Watson, R. T., Chemical kinetics data survey, 8, Rate constants of ClO₂ of atmospheric interest, *NB SIR 74-516*, Nat. Bur. of Stand., Washington, D. C., 1974.

Welge, K. H., Photolysis of O₂, HO₂, CO₂ and SO₂ compounds, *Can. J. Chem.*, *52*, 1424, 1974.

Westenberg, A. A., and N. de Haas, Reinvestigation of the rate coefficients for O + H₂ and O + CH₄, *J. Chem. Phys.*, *50*, 2512, 1969.

Westenberg, A. A., and N. de Haas, Measurement of the rate constant for H + H₂CO → H₂ + HCO at 297-652°K, *J. Phys. Chem.*, *76*, 2213, 1972a.

Westenberg, A. A., and N. de Haas, Relative rate constants for O + HCO → OH + CO and O + HCO → H + CO₂, *J. Phys. Chem.*, *76*, 2215, 1972b.

Westenberg, A. A., and N. de Haas, Rate of reaction of OH + OH → H₂O + O, *J. Chem. Phys.*, *58*, 4046, 1973a.

Westenberg, A. A., and N. de Haas, Rate of CO + OH and H₂ + OH over an extended temperature range, *J. Chem. Phys.*, *58*, 4061, 1973b.

Westenberg, A. A., N. de Haas, and J. M. Roscoe, Radical reaction in an electron spin resonance cavity homogeneous reactor, *J. Phys. Chem.*, *74*, 3431, 1970.

Widing, K. G., J. D. Purcell, and G. D. Sandlin, The UV continuum 1450-2100 Å and the problem of the solar temperature minimum, *Solar Phys.*, *12*, 52, 1970.

Wilkniss, P. E., R. A. Lamontagne, R. E. Larson, J. W. Swinnerton, C. R. Dickson, and T. Thompson, Atmospheric traces in the Southern Hemisphere, *Nature*, *245*, 45, 1973.

Wilkniss, P. E., J. W. Swinnerton, R. A. Lamontagne, and D. J. Bressan, Trichlorofluoromethane in the troposphere, Distribution and increase, 1971 to 1974, *Science*, *187*, 832, 1975a.

Wilkniss, P. E., J. W. Swinnerton, D. J. Bresson, R. A. Lamontagne, and R. E. Larson, CO, CCl₄, Freon-11, CH₄ and Rn-222 concentrations at low altitudes over the Arctic Ocean in January 1974, *J. Atmos. Sci.*, *32*, 158, 1975b.

Willson, R. C., New radiometric techniques and solar constant measurements, *Solar Energy*, *14*, 203, 1973.

Wofsy, S. C., and M. B. McElroy, HO₂, NO₂ and ClO₂: Their role in atmospheric photochemistry, *Can. J. Chem.*, *52*, 1582, 1974.

Wofsy, S. C., J. C. McConnell, and M. B. McElroy, Atmospheric CH₄, CO and CO₂, *J. Geophys. Res.*, *77*, 4477, 1972.

Wofsy, S. C., M. B. McElroy, and N. D. Sze, Freon consumption: Implications for atmospheric ozone, *Science*, *187*, 535, 1975a.

Wofsy, S. C., M. B. McElroy, and Y. L. Yung, The chemistry of atmospheric bromine, *Geophys. Res. Lett.*, *2*, 215, 1975b.

Wong, W., and D. D. Davis, A flash photolysis-resonance fluorescence study of the reaction of atomic hydrogen with molecular oxygen: H + O₂ + M → HO₂ + M, *Int. J. Chem. Kinet.*, *6*, 401, 1974.

Wulf, O. R., and L. S. Deming, The theoretical calculation of the dis-

tribution of photochemically formed ozone in the atmosphere, *J. Geophys. Res., 41*, 299, 1936a.

Wulf, O. R., and L. S. Deming, The effect of visible solar radiation on the calculated distribution of atmospheric ozone, *J. Geophys. Res., 41*, 375, 1936b.

Wulf, O. R., and L. S. Deming, The distribution of atmospheric ozone in equilibrium with solar radiation and the rate of maintenance of the distribution, *J. Geophys. Res., 42*, 195, 1937.

Zahniser, M. S., F. Kaufman, and J. G. Anderson, Kinetics of the reaction of OH with HCl, *Chem. Phys. Lett., 27*, 507, 1974.

Zellner, R., and I. W. M. Smith, Rate constants for the reactions of OH with NH_3 and HNO_3, *Chem. Phys. Lett., 26*, 72, 1974.