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Stratospheric ozone :
An introduction to its study

by

M. NICOLET

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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FOREWORD

"Stratospheric Ozone : An Introduction to its Study" is an invited paper to be published in Review of Geophysics and Space Physics in 1975. It is also reproduced as Scientific Report of the Ionosphere Research Laboratory, The Pennsylvania State University. See additional note following this page.

AVANT-PROPOS

"Stratospheric Ozone : An Introduction to its Study" a été écrit à la demande de l'éditeur de la revue Review of Geophysics and Space Physics. Il est également reproduit comme Scientific Report of the Ionosphere Research Laboratory, The Pennsylvania State University. Voir également la note à la page suivante.

VOORWOORD

"Stratospheric Ozone : An Introduction to its Study" werd geschreven op verzoek van de uitgever van het tijdschrift Review of Geophysics and Space Physics. Deze tekst wordt ook nog uitgegeven als Scientific Report of the Ionosphere Research Laboratory, The Pennsylvania State University. Zie eveneens de nota op de volgende bladzijde.

VORWORT

"Stratospheric Ozone : An Introduction to its Study" wurde geschrieben auf Bitte des Verlegers der Zeitschrift Review of Geophysics and Space Physics. Dieser Text wird auch herausgegeben wie Scientific Report of the Ionosphere Research Laboratory, The Pennsylvania State University. Sehe auch die Notiz auf folgendes Blatt.

Additional Note

"Stratospheric Ozone : An Introduction to its Study" was sent to the Editor of Review of Geophysics and Space Physics in April 1974 and the galley proofs were received and checked at the beginning of September during the "Grenoble Meeting" of the International Union of Geodesy and Geophysics. References of recent publications have been introduced in the galley proofs, event without any discussion, only when it was possible without modifying the original text.

It has been said several times in this article that more precise experimental data are needed even when rate constants are generally accepted. A specific example can be given here before sending this "Aeronomica Acta".

Dr. H. Schiff gave the following results at the Grenoble meeting (afternoon session, IAGA, Wednesday September 3) for the reactions with O(1D) in 10^{-10} cm³ molecule sec⁻¹ at 298 K

N ₂ O	H ₂ O	CH ₄	H ₂	HCl	NH ₃	
1.5	2.1	1.3	1.3	1.4	3.4	Schiff
2.2	3.0	3.1	2.7	---	---	Husain
O ₃	O ₂	N ₂	CO ₂	D ₂		
2.4	0.41	0.30	1.2	1.3		Schiff
2.7	0.7	0.69	2.1	1.8		Husain

The variation with the temperature was also given : with negative activation energy

$$\begin{aligned} \text{O}_2 & ; 2.46 \times 10^{-11} e^{313/RT} \\ \text{N}_2 & ; 1.34 \times 10^{-11} e^{522/RT} \\ \text{CO}_2 & ; 5.13 \times 10^{-11} e^{448/RT} \\ \text{H}_2\text{O} & ; 7.96 \times 10^{-11} e^{511/RT} \end{aligned}$$

and with positive activation energy

$$\begin{aligned} \text{N}_2\text{O} & ; 6.74 \times 10^{-10} e^{-846/RT} \\ \text{H}_2 & ; 5.07 \times 10^{-10} e^{-805/RT} \\ \text{NH}_3 & ; 7.29 \times 10^{-10} e^{-430/RT} \end{aligned}$$

STRATOSPHERIC OZONE : AN INTRODUCTION TO ITS STUDY

by

M. NICOLET

Abstract

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 ppmv, ppbv and pptv ranges may be considered.

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 the 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 depending 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 and other halogens 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 various possibilities of transport. The predictability of the action of chemical reactions depends strongly on important interactions (1) between OH and HO_2 radicals with CO and NO, respectively, and affecting the ratio $n(OH)/n(HO_2)$ at the tropopause level ; (2) between OH and NO_2 leading to the formation of nitric acid with its downward transport towards the troposphere ; (3) between NO and HO_2 leading to NO_2 and its subsequent photodissociation; (4) between ClO and NO leading

also to NO_2 and becoming more important than the reaction of ClO with O , and (5) between Cl and various molecules such as CH_4 , H_2 , .. leading to HCl with its downward transport towards 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.

Résumé

L'objet de ce travail est de procéder à une analyse des diverses réactions qui interviennent dans la formation et la destruction de l'ozone stratosphérique. On a envisagé dans le détail les réactions où interviennent des constituants minoritaires (domaines de concentrations relatives 10^{-6} , 10^{-9} , 10^{-12}) comprenant des atomes d'hydrogène, d'azote et de chlore.

Dans la stratosphère supérieure, au-delà du maximum de concentration de l'ozone, on peut considérer qu'on n'est pas loin des conditions d'équilibre photochimique et que l'action des radicaux OH et HO₂, de NO₂ et du Cl peut être introduite. La détermination précise de leurs effets sur la concentration de l'ozone exige à la fois la connaissance de (1) la distribution verticale de la dissociation de H₂O, CH₄ et H₂ par suite de leur réaction avec l'atome d'oxygène dans l'état excité (O¹D) ; (2) le rapport des concentrations de OH et de HO₂ et de leurs valeurs absolues soumises à l'imprécision des coefficients de réaction ; (3) les diverses origines de la production des oxydes d'azote avec leurs distributions verticales dépendant à la fois de la latitude et des saisons et (4) les diverses sources fournissant les différents composés du chlore et des autres halogènes pouvant être dissociés dans la stratosphère.

Dans la stratosphère inférieure, au-dessous du maximum de la concentration d'ozone, il n'y a pas de production importante de l'ozone par voie photochimique, mais il apparaît différentes possibilités de transport. La possibilité d'action de réactions chimiques est liée à un ensemble d'interactions telles que (1) OH et CO respectivement avec CO et NO; (2) OH avec NO₂ conduisant à la formation de l'acide nitrique avec sa descente vers la troposphère; (3) NO avec HO₂ formant ainsi NO₂ qui après photodissociation donnent des atomes d'oxygène; (4) ClO avec NO donnant lieu encore à NO₂ et étant plus important que ClO avec O et (5) Cl avec CH₄, H₂, ... fournissant HCl qui descend normalement vers la troposphère où il disparaît. Tous ces

processus chimiques varient constamment car ils apparaissent dans la basse stratosphère où l'ozone est soumis à des variations liées à la saison, à la latitude et même apparaissant d'un jour à l'autre. Toutes ces variations doivent être associées à des transports advectifs ou dynamiques qui dépendent des conditions météorologiques comme l'indiquent les variations de la hauteur de la tropopause.

Samenvatting

Het doel van dit werk is een analyse te geven van de verschillende reacties waarbij ozon en atomaire zuurstof in de stratosfeer betrokken zijn. De reacties van de minderheidsbestanddelen (met relatieve concentraties van 10^{-6} , 10^{-9} , 10^{-12}) met waterstof, stikstof en chloor atomen worden besproken.

In de hogere stratosfeer, boven het maximum in de ozonconcentratie, kan men veronderstellen dat het fotochemisch evenwicht bijna bereikt is en kan de werking van de radicalen OH en HO₂, NO₂ en Cl ingevoerd worden. Een juiste bepaling van hun invloed vereist : (1) de verticale verdeling van de dissociatie van H₂O, CH₄ en H₂ tengevolge van hun reactie met atomaire zuurstof in de aangeslagen toestand O(¹D) ; (2) de verhouding van de concentraties van OH en HO₂ en hun absolute waarden afhankelijk van de onnauwkeurigheid waarmede de reactiecoëfficiënten gekend zijn ; (3) de verschillende oorsprongen van de productie der stikstofoxydes met hun verticale distributies afhankelijk van de breedte en de jaargetijden ; en (4) de verschillende bronnen die de chloor verbindingen en andere halogenen leveren die in de stratosfeer gedissociëerd kunnen worden.

In de lage stratosfeer, beneden de ozonpiek, is er geen belangrijke fotochemische productie van O₃ meer, maar bestaan er verschillende transportmogelijkheden. De mogelijkheid voor chemische reacties is afhankelijk van tal van interacties zoals : (1) OH en CO respectievelijk met CO en NO ; (2) OH met NO₂ waarbij HNO₃ gevormd wordt dat naar de troposfeer afzakt ; (3) NO met HO₂ waarbij NO₂ gevormd wordt dat daarna onderworpen is aan fotodissociatie ; (4) ClO met NO met vorming van NO₂ en die belangrijker is dan de interactie van ClO met O ; en (5) Cl met CH₄, H₂,... waarbij HCl gevormd wordt dat afzakt naar de troposfeer. Al deze chemische processen variëren gedurig vermits zij plaats hebben in de lage stratosfeer waar ozon onderworpen is aan de variaties tengevolge van de breedte en jaargetijden.

Al deze variaties staan in verband met advectioneel en dynamisch transport dat afhankelijk is van de meteorologische omstandigheden zoals blijkt uit de variaties van de hoogtes der tropopauze.

Zusammenfassung

Eine Analyse der verschiedenen Reaktionen worin Ozon und Atomsauerstoff eintreten, wird in der Stratosphäre durchgeführt. Die Reaktionen worin Wasserstoff-, Stickstoff- und Chlor- minderheitskomponenten mit relativen Konzentrationen im Gebiet 10^{-6} , 10^{-9} und 10^{-12} eintreten, werden durchaus betrachtet

In der höheren Stratosphäre, oberhalb des Ozonmaximum wo kein starker Unterschied mit dem photochemischen Equilibrium stattfindet, kann die Wirkung der OH und HO₂ Radikalen und NO₂ und Cl eingeführt werden. Eine genaue Bestimmung dieser Wirkung über der Ozonkonzentration erfordert die folgende Kenntnisse : (1) die senkrechte Verteilung der H₂O-, CH₄- und H₂- Dissoziation durch die Reaktion mit angeregtem Atomsauerstoff O(¹D), (2) das Verhältnis zwischen die OH und HO₂ Konzentrationen sowie die absolute Werten, die auf dem Mangel an Genauigkeit der Reaktionskoeffizienten abhängen (3) die verschiedene Ursprünge der Stickstoffoxiden Produktionen sowie die senkrechte Verteilungen die auf der Breite und Jahreszeiten abhängen (4) die verschiedene Quellen der Chlorkomponenten und der anderen Salzbilder, die in der Stratosphäre dissoziiert können werden.

In der niedrigen Stratosphäre, unterhalb des Ozonmaximum, gibt es keine wichtige photochemische Produktion von O₃, aber verschiedene Transportmöglichkeiten erscheinen. Die Möglichkeit einer Wirkung durch chemische Reaktionen hängt von verschiedenen Zwischenwirkungen ab, sowie (1) OH und CO gegenseitig mit CO und NO, (2) OH mit NO₂ die zur Bildung der Salpetersäure mit seinem Hinuntergehen in die Troposphäre führt, (3) NO mit HO₂ die zur Bildung von NO₂ der photodissoziiert wird, führt, (4) ClO mit NO die auch NO₂ produziert und die wichtiger als die Wirkung zwischen ClO und O ist, (5) und Cl mit CH₄, H₂,... die HCl bilden, der in die Troposphäre hinuntergeht und da verschwindet. Alle diese chemischen Wirkungen ändern

immer, weil sie in der unteren Stratosphäre, wo Ozon von der Jahreszeiten, Breite und eben taglichen Variationen abhängt, stattfinden. Diese Variationen müssen mit dynamischen Transporten, die von den meteorologischen Zuständen abhängen, verbunden werden, als die Variationen der Tropopause hohe es zeigen.

INTRODUCTION

The aeronomy and meteorology of atmospheric ozone have been studied by many scientists since the suggestion made by Schoenbein (1840 a,b) of the existence of an atmospheric constituent having a particular odor (from Greek, ozein = to smell) and its exact origin deduced by de 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 made the identification (Hartley 1881b) of 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 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, 1921 a,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 it 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 centred 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 by Craig (1950) for the period before direct soundings made with optical instruments were introduced (Külcke 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, 1970).

To-day, the rocket observations (Krueger, 1973), and particularly the continuous 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 a complete information from a synoptic analysis as it was done by

Piaget (1969, 1971). A great amount of effort is still needed to understand the atmospheric movements in the neighbourhood 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 fifty years.

The photochemical theory put forward by Chapman (1930, 1943) was first developed for a pure oxygen atmosphere (Mecke, 1931; Wulf and Deming, 1936 a,b, 1937; Dütsch, 1946; Craig, 1950) and, therefore, was greatly idealized. However, twenty five years ago, vibrational-rotational bands of the hydroxyl radical OH, which were identified in the airglow, by 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 study of 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 $\text{O}(^1\text{D})$ 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, 1974; Wofsy and McElroy, 1974), its role has been recognized (Clyne and Watson, 1974; Cicerone et al., 1974, 1975b); Crutzen, 1974b; Wofsy et al., 1974) since its possible action has been demonstrated in various papers by Molina and Rowland (1974 a,b) and Rowland and Molina (1975) in which the effect of industrial chlorofluoromethanes 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, their aeronomic properties should be considered with their natural and industrial sources when all experimental rate coefficients are determined. Attention has been focussed recently on atmospheric bromine by Wofsy et al. (1975b).

2. OZONE FORMATION AND DESTRUCTION

In order to describe the stratospheric problems of the 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 (1950) 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 considered by considering the various reactions that are involved in the stratosphere (Nicolet, 1965a ; Crutzen, 1971; Johnston, 1971; Nicolet, 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 (Dr. Garvin and coll.) and will be published in a Monograph of the Climatic Impact Assessment Program, Department of Transportation, Washington D.C.). A publication by Garvin and Hampson (1974) and Hampson and Garvin (1975) gives the principal tables of chemical kinetic and photochemical data for gas phase reactions in the stratosphere.

3. 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) :



A recent laboratory analysis (Campbell and Gray, 1973) at 196 and 298 K leads to a rate coefficient

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

However, such a 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



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

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

Ozone molecules are destroyed by a two-body collision process



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., 1973d) lead to a value which is not too different from

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

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

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

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

$$\frac{dn(O)}{dt} + 2k_1 n(M) n^2(O) + k_2 n(M) n(O_2) n(O) + k_3 n(O_3) n(O) = 2 n(O_2) J_2 + n(O_3) J_3 \quad (5)$$

and

$$\frac{dn(O_3)}{dt} + n(O_3) J_3 + k_3 n(O) n(O_3) = k_2 n(M) n(O_2) n(O) \quad (6)$$

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

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

Introducing the time $\tau_q(O_3)$, necessary to attain 50 percent (or to reach 80 percent from 50 percent) of the photochemical value $n_*(O_3)$, the following equation is obtained

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

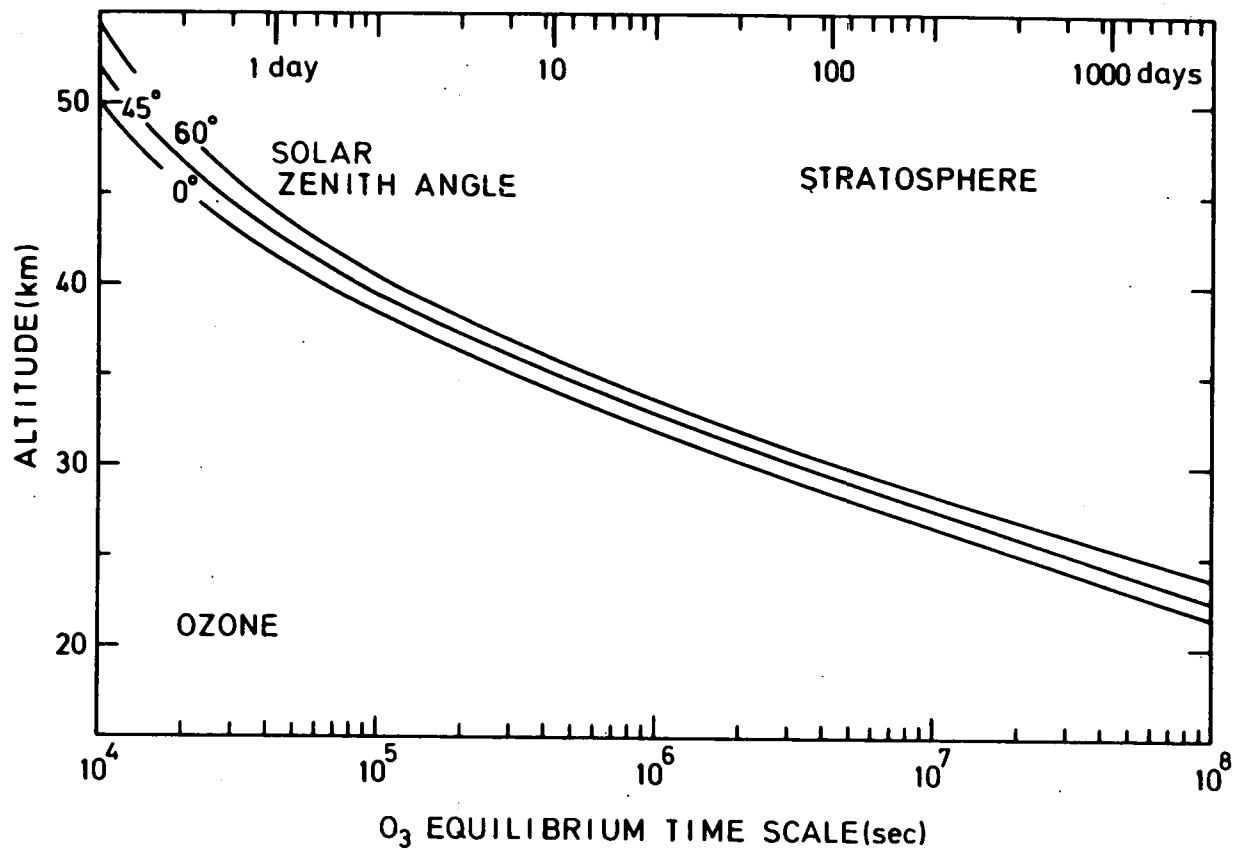


Fig. 1.- Equilibrium time scales for ozone in a pure oxygen atmosphere : less than one day above 45 km, more than one year below 25 km for daytime conditions.

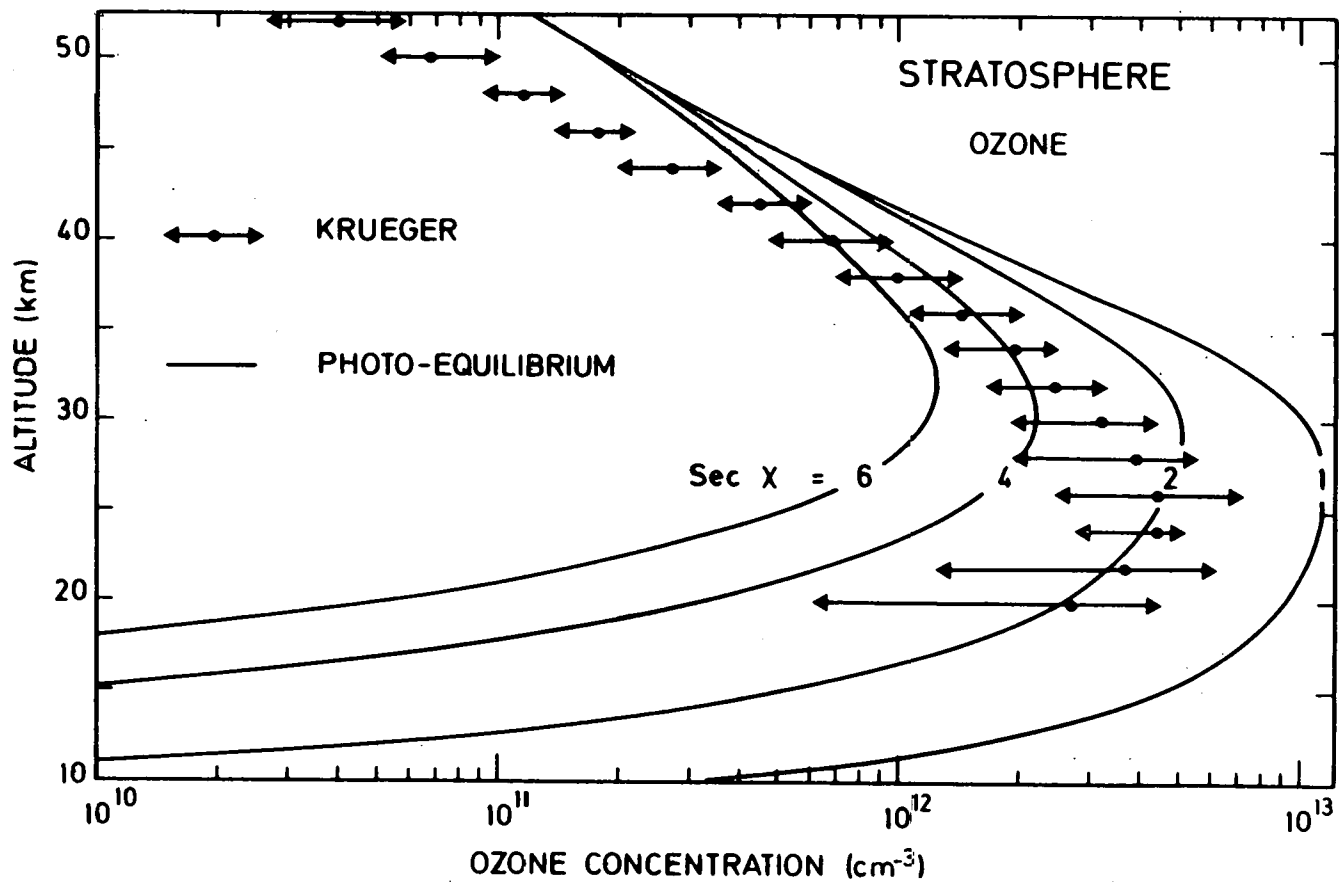


Fig. 2.- Observed and calculated ozone profiles. Calculation for photoequilibrium conditions at various solar zenith angles χ , $\sec \chi = 1, 2, 4$ and 6 . Range in ozone observations of 24 rockets flights between 58° S and 64° N by Krueger (1973).

With numerical values, it can be shown (Fig. 1; Nicolet, 1973) that photochemical equilibrium can be adopted for $n(O_3)$ at the stratopause. From (8), the following equation

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

represents photochemical equilibrium conditions in the upper 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 photoequilibrium 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 (Fig. 2; Nicolet, 1974) 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 per cent 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 .

4. REACTIONS IN A HYDROGEN-OXYGEN ATMOSPHERE

A hydrogen-oxygen atmosphere seems to be very complicated (Bates and Nicolet, 1950c). However, when a analysis of the various reaction rates is made a certain number of them can be ignored and for several years it was assumed (Hunt, 1966; Leovy, 1969, etc) 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

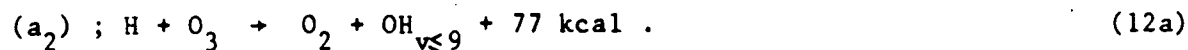


which has the following rate coefficient

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

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,

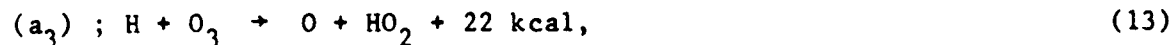


A new value for the rate coefficient has been recently deduced (Clyne and Monkhouse, private communication, 1975) ; it is

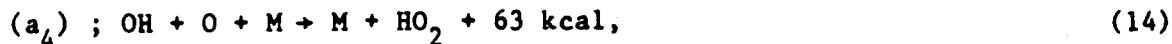
$$a_2 = 1.2 \times 10^{-10} e^{-560/T} \text{ cm}^3 \text{ sec}^{-1} \quad (12b)$$

leading to $1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at the stratopause.

The production of hydroperoxyl radicals by



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



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

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



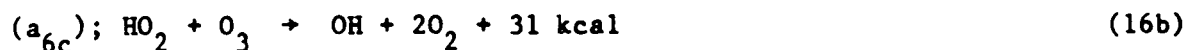
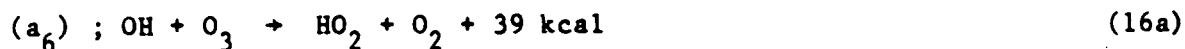
Laboratory data (Clyne and Thrush, 1963; Kaufman, 1964, 1969 ; Breen and Glass, 1970; Westenberg et al., 1970) indicate possible values between 2 and $7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. A value such as

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

may be considered as a working value with a possible error of ± 50 per cent.

It is clear that, if the effects of (15) are important in the mesosphere and also 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



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

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

leads to $5.5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at room temperature (Anderson and Kaufman, 1973) and to 1 to $2 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at temperatures of the lower stratosphere. Such values are less (by more than a factor of ten) 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

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

may be considered as an acceptable average value between the values obtained by Simonaitis and Heicklen (1973b) and DeMore and Tschuikow-Roux (1974). Such a value of the rate coefficient leads to $3 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ 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 :



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 re-formation of oxygen molecules. There is no special support for any value

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

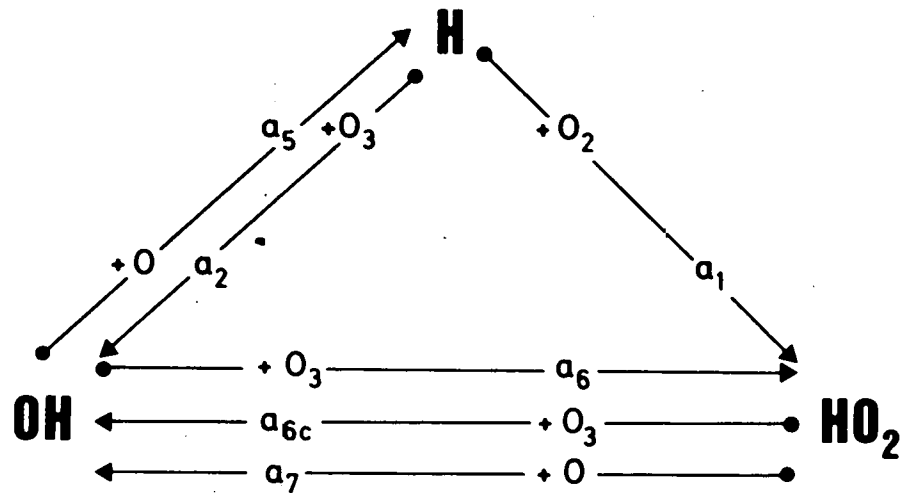


Fig. 3.- Reaction scheme of H, OH and HO₂ showing their interconnection at the stratopause.

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.



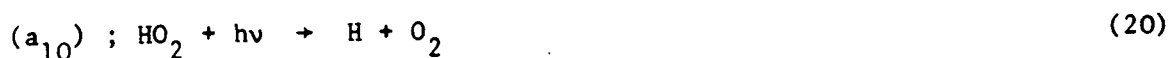
Such a reaction will be ignored ($a_8 = 0$), even if there is a possibility of a dissociation due to the predissociation of the $A^2\Sigma^+$ state for levels $v' > 0$.

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



It is certain that the photodissociation process (19) is less important than reaction (17) in the upper stratosphere.

As for the photodissociation process



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 $n(\text{OH})/n(\text{H})$ and $n(\text{HO}_2)/n(\text{H})$ (Fig. 3) can be easily obtained for the stratopause level and the upper stratosphere since only a limited number of reactions is involved. Thus,

$$\frac{n(\text{OH})}{n(\text{H})} = \frac{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)}{a_5 n(\text{O})} \quad (21)$$

$$\frac{n(\text{HO}_2)}{n(\text{H})} = \frac{a_1 n(\text{M}) n(\text{O}_2)}{a_7 n(\text{O})} \quad (22)$$

and

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)}{a_1 n(\text{M}) n(\text{O}_2)} \cdot \frac{a_7}{a_5} \quad (23)$$

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

$$n^2(\text{O}_3) = \frac{k_2}{k_3} n(\text{M}) n^2(\text{O}_2) \frac{J_3}{J_3(1 + A)} \quad (24)$$

with the correction term

$$A = \frac{a_5 n(\text{OH}) + a_7 n(\text{HO}_2)}{2 k_3 n(\text{O}_3)} \quad (25)$$

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

$$\frac{dn(O_3)}{dt} + n(O_3) [2k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2)] = 2 n(O_2) J_2 \quad (26)$$

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

$$\frac{n(OH)}{n(HO_2)} = \frac{a_{6c}}{a_6} = \frac{(3 \pm 1) \times 10^{-16}}{(1.3 \pm 0.5) \times 10^{-14}} = \frac{1}{50} \quad (27)$$

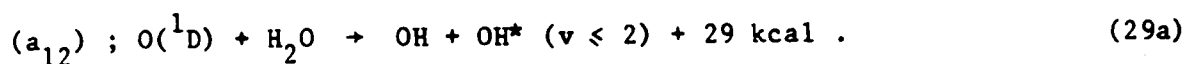
at a temperature of the order of 210 ± 10 K.

With a negligible production of ozone at this level (with no transport involved), a reduction in two months the ozone concentration to 50 per cent 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. The photodissociation of H_2O which leads to



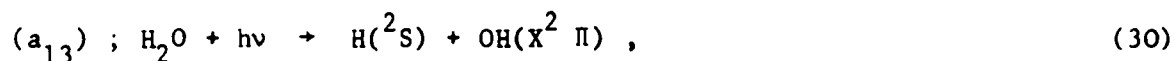
is a mesospheric process above 70 km due to the effect of solar Lyman- α at 121.6 nm. If an effect on H_2O caused by oxygen atoms in their normal state ^3P has not been detected because the reaction was endothermic, an important process will occur with oxygen atoms in their first excited state ^1D , (Engleman, 1965) :



for which a relatively precise value can be adopted

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

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



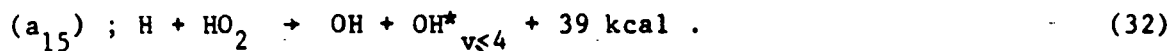
which can still occur in the stratosphere, is less important than the reaction process (29).

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



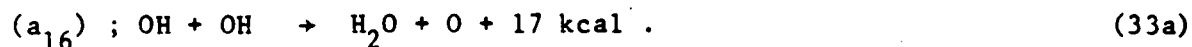
which can be neglected when it is compared with other possible aeronomic processes such as a_{16} and a_{17} .

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



This reaction has been observed (Cashion and Polanyi, 1959) but it is not yet possible to find a sufficiently 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_{23} and their ratios indicate the difficulty in adopting correct values.

The reaction between two hydroxyl radicals leads to the re-formation of water vapor



If recent laboratory measurements (Westenberg and de Haas, 1973a; Trainor and von Rosenberg, 1974a; Clyne and Down, 1974) are considered, $T = 300 \text{ K}$, the following value is adopted :

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

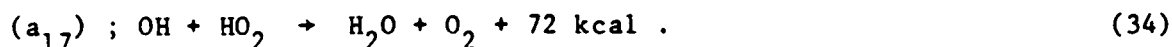
In addition to the two-body process (33), the three-body association



must be introduced with the rate coefficient (Trainor and von Rosenberg, 1974a)

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

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



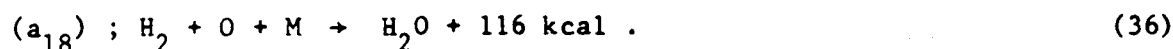
Laboratory results by Hochanadel et al. (1972) lead to a very high value of the rate coefficient

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

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

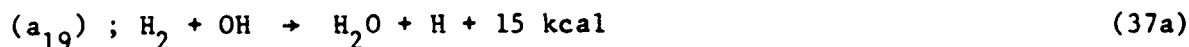
important cause of re-formation of water vapor in the stratosphere. However, if a much lower value is used such as suggested by Kaufman (1974) and given by Hack *et al.* (1975), the determination of the OH + HO₂ concentration remains an unresolved problem.

Other reactions can lead to the formation of H₂O, but they are not as important in the stratosphere as the reactions that lead to its re-formation. The three-body association



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 H₂ and OH

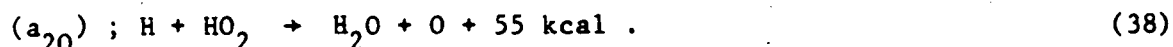


requires a relatively high activation energy (Greiner, 1969). A recent laboratory measurement (Smith and Zellner, 1974) between 210 and 410 K results in

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

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 H₂O



The rate coefficient a_{20} should be of the same order of magnitude as a_{15} , 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 conditions in a pure oxygen-hydrogen atmosphere

$$n(H_2O) a_{12}^* n(O^*) = a_{20} n(H) n(HO_2) + n(OH) [a_{16} n(OH) + a_{17} n(HO_2) + a_{19} n(H_2)] . \quad (39a)$$

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

$$n(OH) [a_{16} n(OH) + a_{17} n(HO_2) + a_{30} n(H_2O_2) + c_2 \left(\frac{1 - X}{2} \right) n(CH_4) + b_{27} n(HNO_3)] = a^* n(O^*) [n(H_2O) + n(H_2) + \frac{1 + X}{2} n(CH_4)] . \quad (40)$$

To obtain such an equation it is necessary to a 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 ppmv), cannot be completely neglected in the stratosphere and its observation may lead to the understanding of stratospheric aeronomic processes. It is formed by a three-body association of two hydrogen atoms



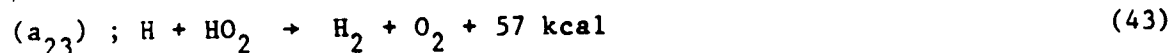
which can be neglected in comparison with bimolecular processes. The reaction



requires a high activation energy (Bausch et al., 1972)

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

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



for which a precise rate coefficient is not available. This reaction, which occurs with a_{15} and a_{20} , has an important role in the mesosphere ; it can produce molecular hydrogen which may be transported downwards into the stratosphere.

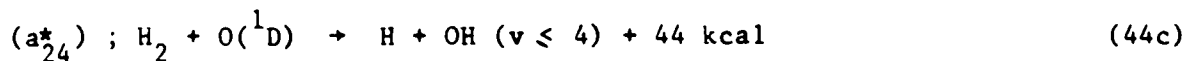
The destruction process



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

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

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



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

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

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

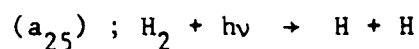
$$\frac{dn(\text{H}_2)}{dt} + n(\text{H}_2) [a_{24}^* n(\text{O}^*) + a_{19} n(\text{OH})] = n(\text{H}) n(\text{HO}_2) a_{23} . \quad (45)$$

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

$$\frac{\partial n(\text{H}_2)}{\partial t} + \frac{\partial [n(\text{H}_2) w(\text{H}_2)]}{\partial z} + n(\text{H}_2) [a_{24}^* n(\text{O}^*) + a_{19} n(\text{OH})] = n(\text{H}) n(\text{HO}_2) a_{23} \quad (46)$$

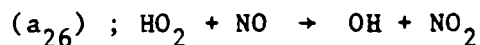
where w is the diffusion velocity. Stratospheric H_2 depends not only on its concentration in the troposphere (the lower boundary condition) and upward vertical transport but also on possible downward transport from the mesosphere, where there is a production source. Also, H_2 can be produced by reactions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

The photodissociation of molecular hydrogen



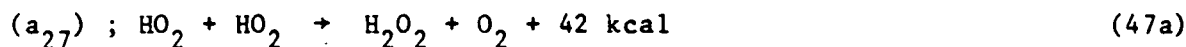
does not occur below 100 km and is therefore neglected.

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



in the stratosphere should be kept in mind before reaching any final conclusion; see 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



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

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

according to Hochanadel et al. (1972), or

$$a_{27} = (3.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (47c)$$

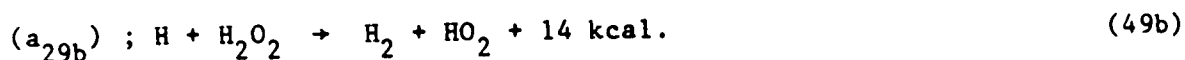
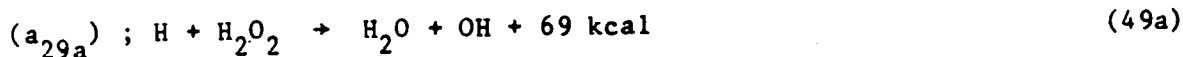
according to Paukert and Johnston (1972). In order to obtain a correct evaluation of the various effects of this important reactions other experimental determinations are needed.

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

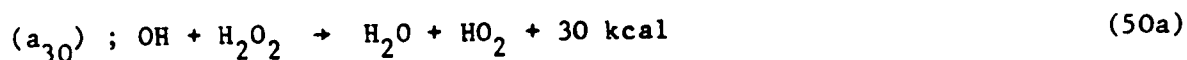


The variation of the photodissociation coefficient $J_{\text{H}_2\text{O}_2}$ with the solar angle is particularly important in the lower stratosphere where its value decrease to $10^{-6} \leq J_{\text{H}_2\text{O}_2} < 10^{-5} \text{ sec}^{-1}$.

The reaction with atomic hydrogen leads to



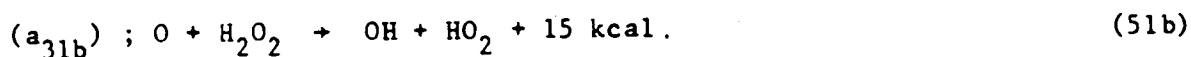
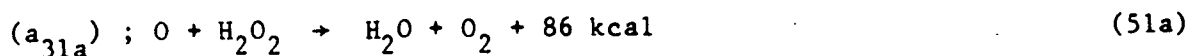
Experimental evidence (Klemm et al., 1975; Gorse and Volman, 1974) indicates that the role of (49) in the stratosphere is not important. But the reaction between a hydroxyl radical and hydrogen peroxide



is important since its rate coefficient is of the order of $1 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ 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

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

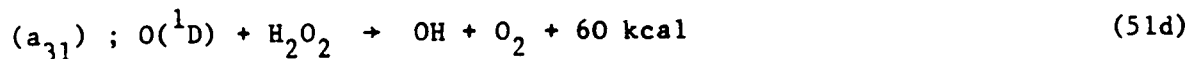
and will result in a rate of about $5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ in the lower stratosphere. Finally, the reaction between oxygen atoms and hydrogen peroxide molecules will be considered since atomic oxygen is an important minor constituent of the stratosphere.



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

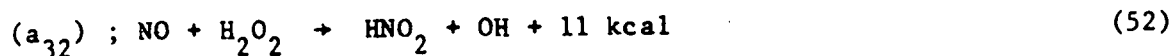
$$a_{31} = 2.75 \times 10^{-12} e^{-2125/T} \text{ cm}^3 \text{ sec}^{-1} \quad (51c)$$

leading to a value of about $1 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ 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 $\text{O}({}^1\text{D}) - \text{H}_2\text{O}_2$ reactions such as

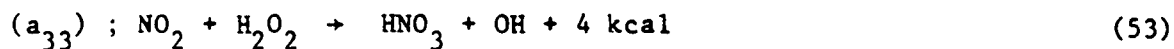


with a rate coefficient of the order of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. However, like (51a), it is a very slow loss process of hydrogen peroxide.

Hydrogen peroxide could react with nitrogen oxides ; for example,

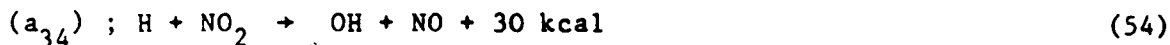


This reaction is negligible (see reaction b_{30}) like



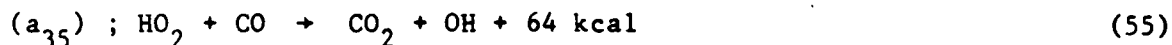
which is not used in stratospheric aeronomy (Gray et al., 1972).

Various rapid reactions such as

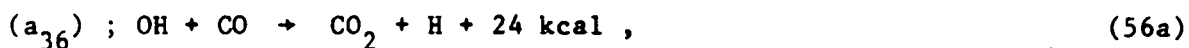


can be neglected since other reactions (here $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$) are always more important. However, two reactions with carbon monoxide must be considered.

The first



is, however, without importance since $a_{35} < 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$ (Simonaitis and Heicklen, 1973b; Davis et al., 1973c). As far as the reaction with OH is concerned



it can play a role in the lower stratosphere since its rate coefficient (Greiner, 1969; Smith and Zellner, 1973; Westenberg and deHaas, 1973b ; Davis et al., 1973a; Trainor and von Rosenberg, 1974b) is

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

in the lower stratosphere. The limiting value would be, according to Sie et al. (1975a), at 300 K,

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

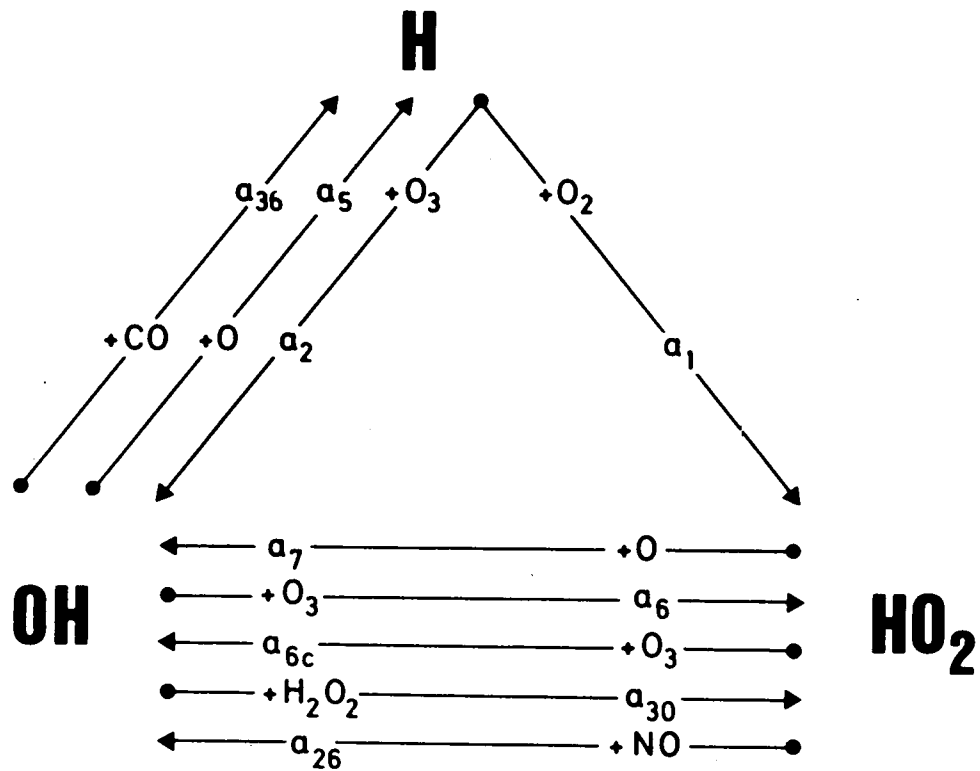


Fig. 4.- Partial reaction scheme of H, OH and HO₂ indicating the complexity of their interactions, particularly in the lower stratosphere.

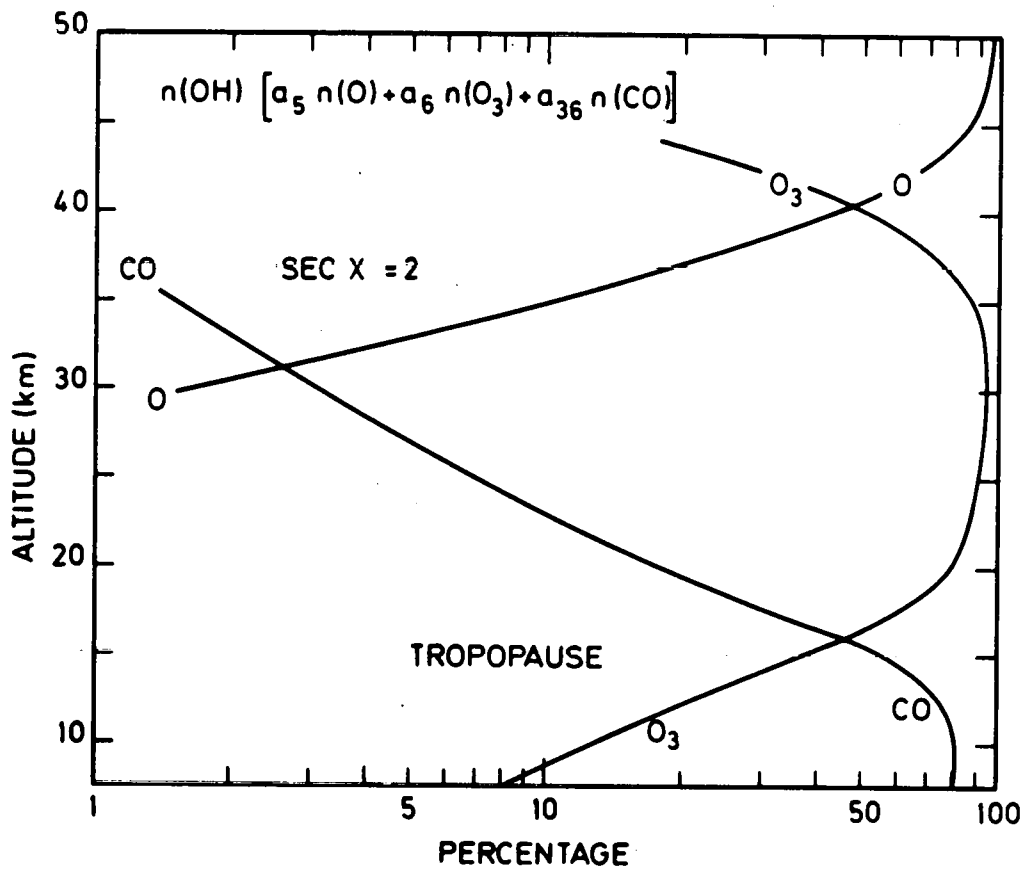


Fig. 5.- Profiles (%) of various terms affecting OH in the determination of the ratio $n(\text{HO}_2)/n(\text{OH})$; to be considered as examples.

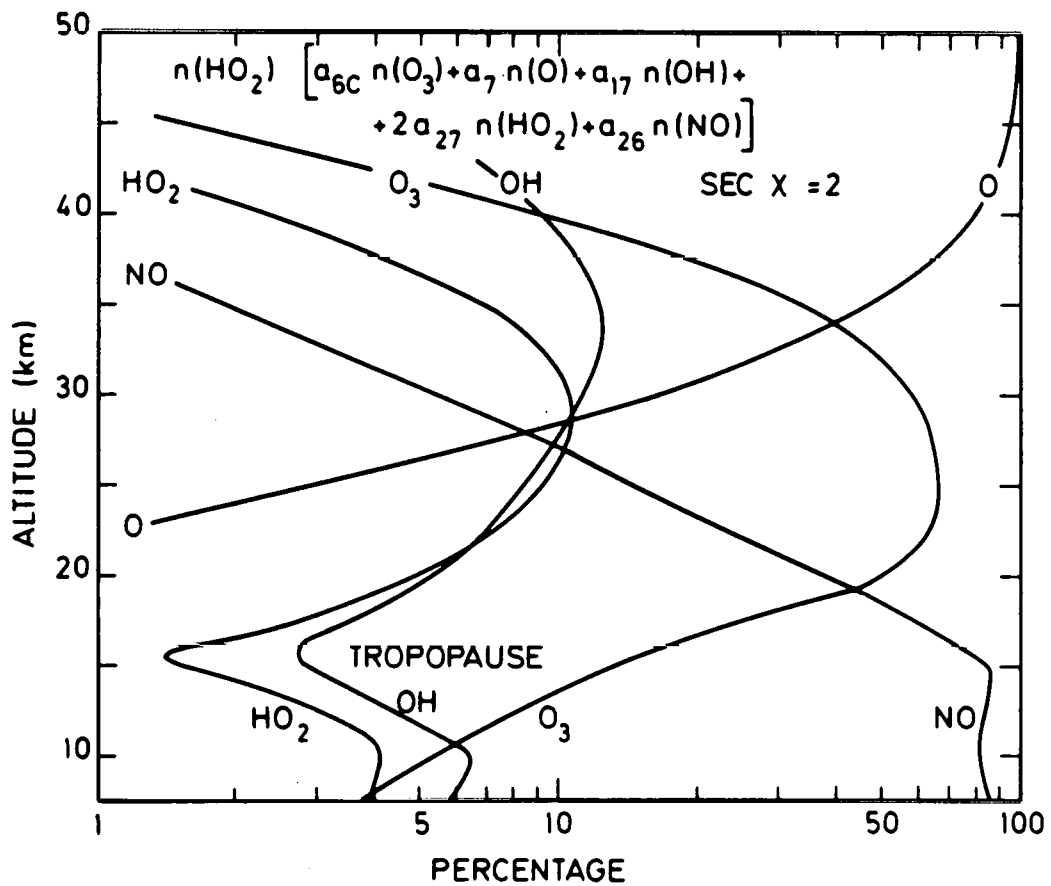


Fig. 6.- Profiles of various terms affecting HO_2 in the determination of the ratio $n(\text{HO}_2)/n(\text{OH})$; to be considered as examples.

If only important reactions (Fig. 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 $n(\text{OH})/n(\text{HO}_2)$ can be written :

$$\begin{aligned} n(\text{HO}_2) & [a_{6c} n(\text{O}_3) + a_7 n(\text{O}) + a_{17} n(\text{OH}) + 2 a_{27} n(\text{HO}_2) + a_{26} n(\text{NO})] \\ & = n(\text{OH}) [a_5 n(\text{O}) + a_6 n(\text{O}_3) + a_{19} n(\text{H}_2) + a_{30} n(\text{H}_2\text{O}_2) + a_{36} n(\text{CO})] \end{aligned} \quad (57)$$

With the aim of illustrating the day equilibrium represented by (57) two figures have been prepared. In Fig. 5, the various percentages of the different coefficients affecting $n(\text{OH})$ are given (Nicolet, 1974). In the upper troposphere and lower stratosphere the dominant path transforming OH to $\text{H} + \text{HO}_2$ 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 $\text{H} + \text{HO}_2$ 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 Fig. 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 per cent of the reactions with OH, HO_2 and O. Thus, the main features of Fig. 5 and 6 correspond to the effect on OH and HO_2 of atomic oxygen at the stratopause and in the upper stratosphere, 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 $n(\text{OH})/n(\text{HO}_2)$ 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

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)}{a_1 n(\text{M}) n(\text{O}_2)} \cdot \frac{a_7}{a_5} \quad (58)$$

and, in the lower stratosphere for daytime conditions, we have

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_{6c} n(\text{O}_3) + a_{26} n(\text{NO})}{a_6 n(\text{O}_3) + a_{36} n(\text{CO})} \quad (59)$$

and for a low tropopause

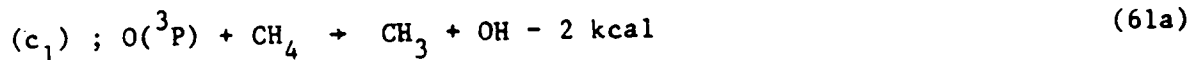
$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_{26} n(\text{NO})}{a_{36} n(\text{CO})} \quad (60)$$

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 $n(\text{OH})/n(\text{HO}_2)$ 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 $\text{OH} + \text{HO}_2$ (a_{17}), $\text{HO}_2 + \text{HO}_2$ (a_{27}), $\text{O} + \text{HO}_2$ (a_7), $\text{NO} + \text{HO}_2$ (a_{26}) and $\text{H} + \text{HO}_2$ (a_{15} , a_{20} and a_{23}) in order to determine their rate coefficients with accuracy.

5. 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.

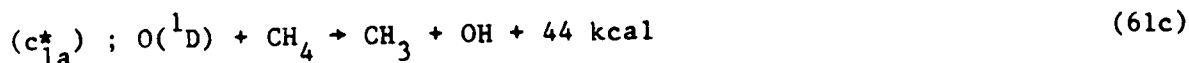
Atomic oxygen attacks methane (see for example Nicolet, 1974) through



which, endothermic by about 2 kcal, is a slow reaction. Its rate coefficient, which is not known with precision, is only about (Westenberg and deHaas, 1969)

$$c_1 = 3.3 \times 10^{-11} e^{-4600/T} \text{ cm}^3 \text{ sec}^{-1} . \quad (61b)$$

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



and also



which occurs to the extent of about 10% (Lin and DeMore, 1973b). The total rate coefficient for $O(^1D)$ (Greenberg and Heicklen, 1972; Heidner and Husain, 1973; Cvetanovic, 1974) is

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

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

The other important reaction in the stratosphere is

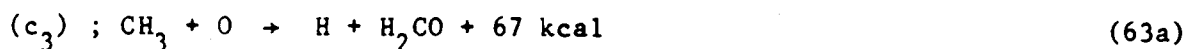


with a well defined rate coefficient

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

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

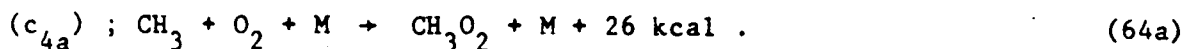
Methyl radicals, which are produced by oxidation processes of CH_4 , may react rapidly with atomic oxygen



with a rate coefficient (Slagle et al., 1974; Washida and Bayes, 1973)

$$c_3 = 1.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} . \quad (63b)$$

This reaction should be important in the mesosphere, but in the stratosphere, methyl radicals react by a three-body process with molecular oxygen



The rate coefficient with $\text{M} \equiv \text{N}_2$ is (Basco et al., 1972)

$$c_{4a} = 2.6 \times 10^{-31} n(\text{N}_2) \text{ cm}^3 \text{ sec}^{-1} \quad (64b)$$

with a limiting value at 300 K

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

The following reaction must also be considered



where the rate coefficient is (N. Washida and K.D. Bayes, private communication, 1975)

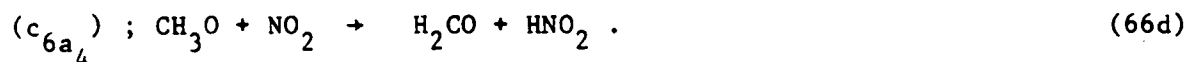
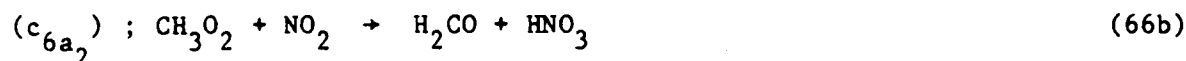
$$c_{4b} = 6.5 \times 10^{-13} e^{-1090/T} \text{ cm}^3 \text{ sec}^{-1} \quad (64e)$$

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



i.e. an oxidation of NO to NO₂. No numerical value is available for the rate coefficient (see Levy 1972, 1973 who has adopted $c_{5a} > 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$).

CH₃O₂ and CH₃O could react with NO₂ (Heicklen, private communication 1975) to produce HNO₃ and HNO₂, respectively.



The ratio $c_{6a2}/(c_{6a1} + c_{6a2})$ would be about 0.25 and $c_{6a4}/(c_{6a4} + c_{6a3}) = 0.08$. A new analysis is required, since it is extremely important to determine the behavior of nitrogen oxides in the lower stratosphere. If $\text{O}(^3\text{P}) + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_2\text{O} + (\text{O}_2 + \text{H})$ has a rate coefficient greater than $3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (N. Washida and K.D. Bayes, private communication, 1975), it should be added to reaction c_5 and c_6 .

The photodecomposition of formaldehyde (McGuigg and Calvert, 1969 ; Calvert et al., 1972; Sperling and S. Toby, 1973; Osif and Heicklen, private communication, 1975) proceeds by radical and molecular paths,

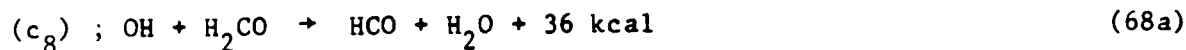


and



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 lead to HO_2 and of the generation of hydrogen molecules in the stratosphere the relative and absolute importance of the dissociation coefficients $J_{\text{HCO-H}}$ and $J_{\text{CO-H}_2}$ must be known with precision.

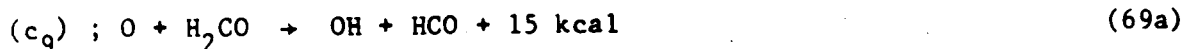
A rapid reaction such as



must be also introduced since (Morris and Niki, 1971) its rate coefficient at 300 K is

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

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



with a rate coefficient (Herron and Penzhorn, 1969; Mack and Thrush, 1973) at 300 K of

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

The reaction with atomic hydrogen is still less rapid



with (Ridley et al., 1972; Westenberg and DeHaas, 1972a)

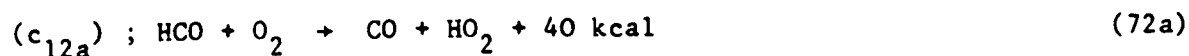
$$c_{10} = 2.2 \times 10^{-11} e^{-1880/T} \quad (70b)$$

i.e. $c_{10} = 4 \text{ to } 5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ 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)



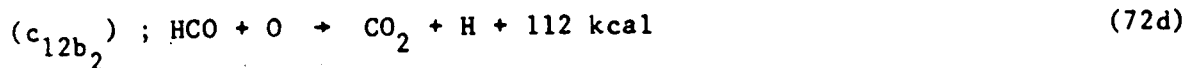
but reacts also with molecular and atomic oxygen :



with a relatively high rate coefficient (Washida et al., 1974)

$$c_{12a} = 5.7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (72b)$$

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



even with a high rate coefficient (Washida et al., 1974)

$$c_{12b} = 2.1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (72e)$$

The ratio c_{12b_1}/c_{12b_2} would be 1.4 according to Westenberg and deHaas (1972b) and about 1 according to Mack and Thrush (1973).

The reaction of HCO with OH is also rapid (Morris and Niki, 1971)

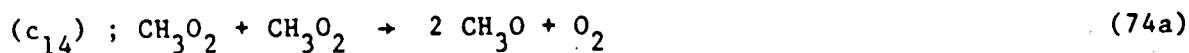


with

$$c_{13} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (73b)$$

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) :



with (Parkes et al., 1973)

$$c_{14} = 3.3 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1} \quad (74b)$$

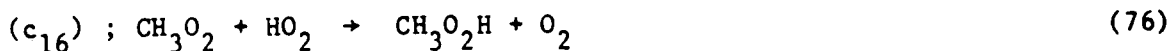
which would be comparable with c_5 for concentrations of NO and CH_3O_2 of the same order of magnitude. It may be neglected in a first analysis ; nevertheless, the removal of CH_3O can be considered by the reaction with O_2



with a slow rate coefficient (Heicklen, unpublished 1975) of the order of

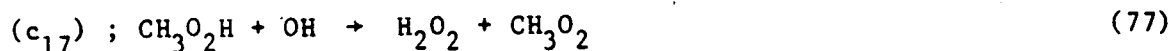
$$c_{15} = 1.6 \times 10^{-13} e^{-3300/T} \quad (75b)$$

to lead to a life time of CH_3O of the order of a few hundreds to one thousand seconds in the lower stratosphere. However, it is necessary to consider the possible effect of HO_2 on CH_3O_2 as follows :



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.

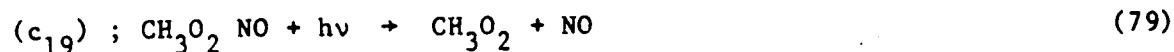
According to Levy (1972), $\text{CH}_3\text{O}_2\text{H}$ reacts either with OH



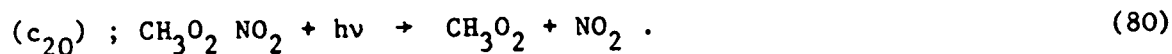
or is subject to photodissociation



Finally, if methylperoxynitrite and methylperoxynitrate are formed, the photodissociation should be considered to be



and



Reactions of CH_3 , CH_3O and CH_3O_2 with ozone have also been considered (Simonaitis and Heicklen, 1975a). The experimental results are



with

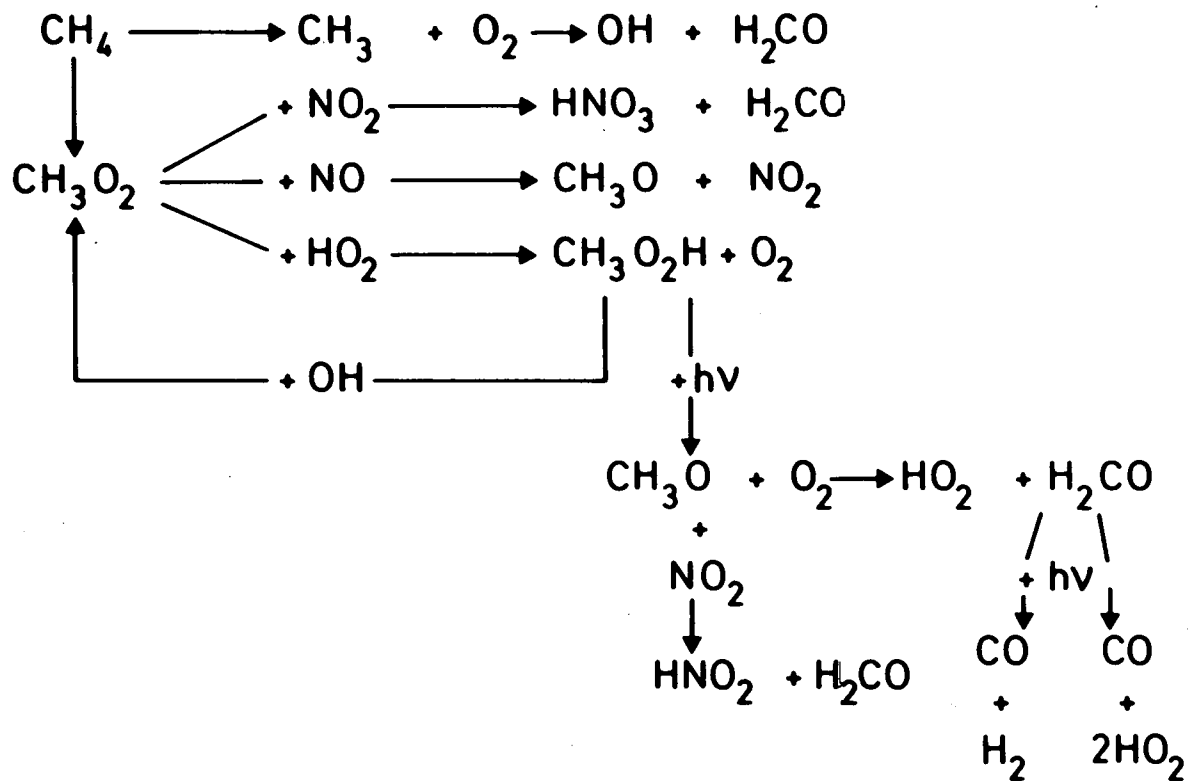


Fig. 7.- Reaction scheme of the dissociation of methane in the stratosphere leading to the production of carbon monoxide.

$$c_{21} = 5.4 \times 10^{-12} e^{-525/T} \quad (81b)$$

and lead to a value of the order $5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ 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 $< 2 \times 10^{-15}$ and $< 2.4 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$, 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). Fig. 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_x 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

$$\begin{aligned} n(\text{H}_2\text{CO}) [J_{\text{H-HCO}} + J_{\text{H}_2-\text{CO}} + c_8 n(\text{OH}) + c_9 n(\text{O}) + c_{10} n(\text{H})] \\ = n(\text{CH}_4) [c_1 n(\text{O}) + c_{1a}^* n(\text{O}^*) + c_2 n(\text{OH})] \\ = n(\text{HCO}) [J_{\text{H-CO}} + c_{12} n(\text{O}_2) + c_{13} n(\text{OH})] + n(\text{H}_2\text{CO}) J_{\text{H}_2-\text{CO}} \end{aligned} \quad (82)$$

and with the principal reactions

$$n(\text{H}_2\text{CO}) [J_{\text{H-HCO}} + J_{\text{H}_2\text{-CO}} + c_8 n(\text{OH})] = n(\text{CH}_4) [c_{1a}^* n(\text{O}^*) + c_2 n(\text{OH})] =$$

$$n(\text{HCO}) c_{12} n(\text{O}_2) + n(\text{H}_2\text{CO}) J_{\text{H}_2\text{-CO}} . \quad (83)$$

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 HO₂ in CH₄ stratospheric aeronomy, we may write

$$\frac{dn(\text{H})}{dt} + \frac{dn(\text{OH})}{dt} + \frac{dn(\text{HO}_2)}{dt} + n(\text{OH}) [c_2 n(\text{CH}_4) + 2c_{13} n(\text{HCO}) +$$

$$2c_{17} n(\text{CH}_3\text{O}_2\text{H})] = n(\text{CH}_4) [c_1 n(\text{O}) + c_{1a}^* n(\text{O}^*)] +$$

$$2 n(\text{H}_2\text{CO}) J_{\text{H-HCO}} + n(\text{CH}_3\text{O}) c_{15} n(\text{O}_2) . \quad (84)$$

With conditions (83), equation (84) becomes

$$\frac{dn(\text{H})}{dt} + \frac{dn(\text{OH})}{dt} + \frac{dn(\text{HO}_2)}{dt} + n(\text{OH}) c_2 n(\text{CH}_4) [1 - X] +$$

$$2 n(\text{OH}) [c_{13} n(\text{HCO}) + c_{17} n(\text{CH}_3\text{O}_2\text{H})] =$$

$$n(\text{CH}_4) [c_1 n(\text{O}) + c_{1a}^* n(\text{O}^*)] [1 + X] + n(\text{CH}_3\text{O}) c_{15} n(\text{O}_2) \quad (85)$$

with

$$X = \frac{2 J_{\text{H-HCO}}}{J_{\text{H-HCO}} + J_{\text{H}_2\text{-CO}} + c_8 n(\text{OH})} . \quad (86)$$

If laboratory measurements (Sperling and Toby, 1973; Osif and Heicklen, private communication, 1975) which seem to indicate that $J_{\text{H-HCO}} > J_{\text{H}_2\text{-CO}} + c_8 n(\text{OH})$, 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 equation (85) would lead to

$$2 n(\text{OH}) [c_{13} n(\text{HCO}) + c_{17} n(\text{CH}_3\text{O}_2\text{H})] =$$

$$n(\text{CH}_4) \left\{ [c_1 n(\text{O}) + c_{1a}^* n(\text{O}^*)] [X + 1] + c_2 n(\text{OH}) [X - 1] \right\} \quad (87)$$

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

$$n(\text{OH}) [a_{16} n(\text{OH}) + a_{17} n(\text{HO}_2) + a_{30} n(\text{H}_2\text{O}_2) + 2 c_{13} n(\text{HCO}) + 2 c_{17} n(\text{CH}_3\text{O}_2\text{H})]$$

$$= [n(\text{H}_2\text{O}) a_{12}^* + n(\text{H}_2) a_{24}^* + c_{1a}^* n(\text{CH}_4) \frac{1+X}{2}] n(\text{O}^*) + c_2 \left[\frac{X-1}{2} \right] n(\text{CH}_4) n(\text{OH}). \quad (88)$$

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

$$\frac{\partial n(\text{H}_2)}{\partial t} + \frac{\partial n(\text{H}_2)w}{\partial z} + n(\text{H}_2) [a_{24}^* n(\text{O}^*) + a_{14} n(\text{OH})]$$

$$= c_{1b}^* n(\text{O}^*) n(\text{CH}_4) + n(\text{H}_2\text{CO}) c_{7b} + a_{23} n(\text{H}) n(\text{HO}_2). \quad (89)$$

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

$$a_{17} n(\text{OH}) n(\text{HO}_2) = a^* n(\text{O}^*) \left[n(\text{H}_2\text{O}) + n(\text{H}_2) + \frac{3}{2} n(\text{CH}_4) \right]$$

$$+ \frac{1}{2} c_2 n(\text{OH}) n(\text{CH}_4). \quad (90)$$

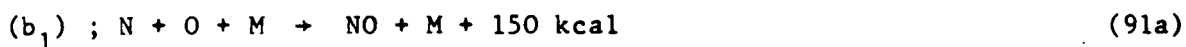
This equation represents the principal production processes of OH and HO₂ radicals that lead to the formation of stratospheric H₂O in a hydrogen-oxygen atmosphere involving methane. Nevertheless, it must be pointed out that the complex interactions among the various reactions require a more reliable data base in order to determine accurately their final action on the stratospheric ozone, particularly in the lower stratosphere.

6. 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 O₂ to form nitric oxide molecules. In the stratosphere, the reaction of the electronically excited oxygen atom O(¹D) with N₂O (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; Basseur and Nicolet, 1973; Nicolet, 1975) must be also considered as an additional source, particularly at mean and high latitudes (geomagnetic latitude $\phi > 45^\circ$). 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 ; etc) which indicate that statistical analyses must be combined with a knowledge of physical processes.

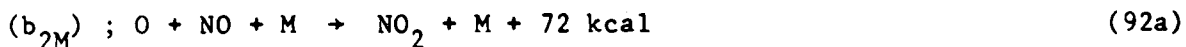
The formation of nitric oxide can be due to a three-body process



with a rate coefficient

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

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 which are the principal active constituents of the chemosphere. First, there is the three-body process



with a relatively high rate coefficient recommended by Baulch et al. (1973)

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

and a limiting value at high pressure and room temperature (Gaedtke and Troe, 1975)

$$b_{2M^{\infty}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} . \quad (92c)$$

This three-body process leading to the formation of nitrogen dioxide must be compared with the radiative process



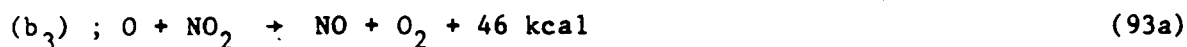
which leads, according to Becker et al. (1972), at low pressure, to the following value of the rate coefficient

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

becoming, according to the results of Golde et al. (1973),

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

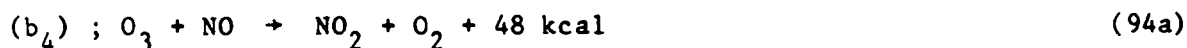
Two bimolecular processes must be considered as essential aeronomic reactions. One is the reaction with oxygen atoms



which is a relatively rapid reaction almost independent of temperature (Davis et al., 1973 ; Slanger et al., 1973 ; Bemand et al., 1974). The following rate coefficient (average value) may be adopted

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

The other reaction of nitric oxide with ozone



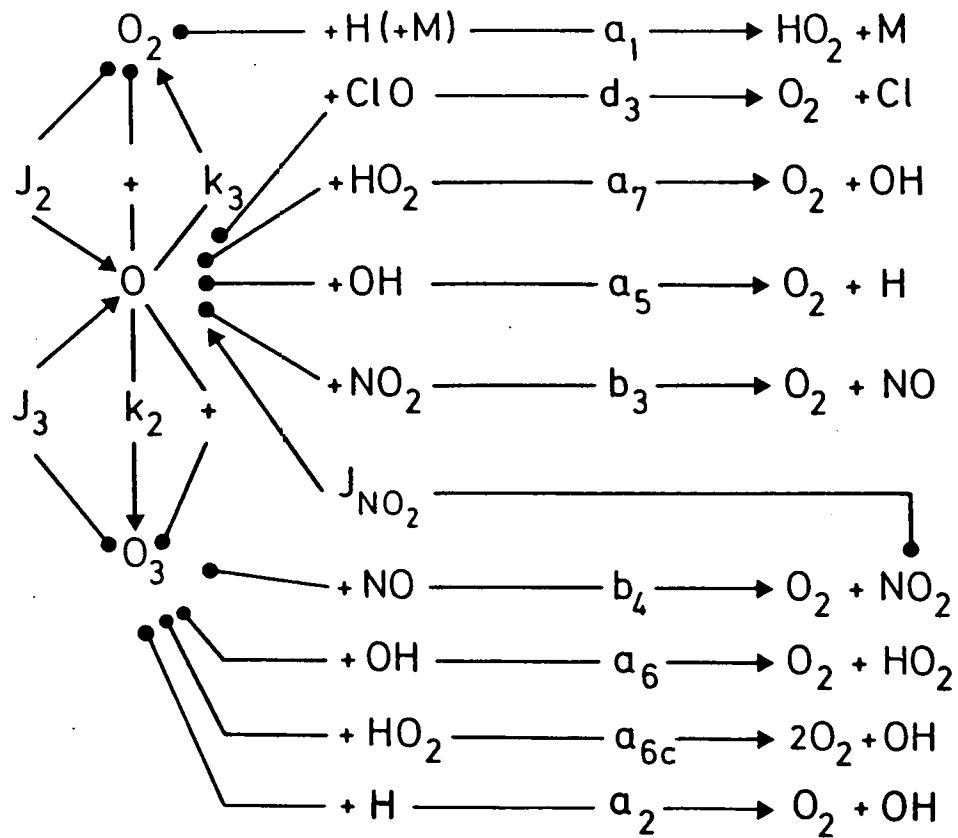


Fig. 8.- Reactions occurring in a nitrogen-hydrogen-oxygen atmosphere that are related to the production and loss of odd oxygen.

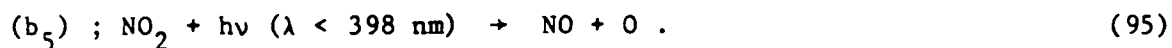
has an activation energy leading to about $(1.8 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at 300 K according to various laboratory measurements and (Johnston and Crosby, 1954; Clyne et al., 1964) to

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

Unpublished results (Huie, Herron and Brown, 1975) give almost the same values, except at low temperature (200 K),

$$b_4 = 3.5 \times 10^{-12} e^{-1530/T} \text{ cm}^3 \text{ sec}^{-1} . \quad (94c)$$

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



Since the life time in the solar radiation field of NO_2 molecules is $200 < \tau_{\text{NO}_2} < 100$ seconds, a photoequilibrium (Nicolet 1955a) must, therefore, exist and leads to the ratio $n(\text{NO}_2)/n(\text{NO})$

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_2 n(\text{O}) + b_4 n(\text{O}_3)}{J_{\text{NO}_2} + b_3 n(\text{O})} \quad (96)$$

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

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_4 n(\text{O}_3)}{J_{\text{NO}_2}} . \quad (97)$$

The scheme of the principal reactions related to the photochemistry of $\text{O} - \text{O}_3$ in the stratosphere is given in Fig. 8 which corresponds to the following equation [see (20), (24), (26) and (96)]

$$\frac{dn(O_3)}{dt} + n(O_3) [a_6 n(OH) + a_{6c} n(HO_2)] + n(O) [2k_3 n(O_3) + a_5 n(OH) + a_7 n(HO_2) + 2b_3 n(NO_2)] = 2n(O_2) J_2 \quad (98)$$

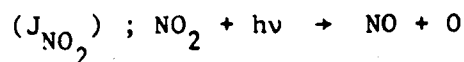
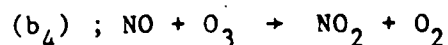
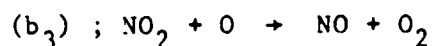
which shows that the correction term for the photoequilibrium region in the equation

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

is

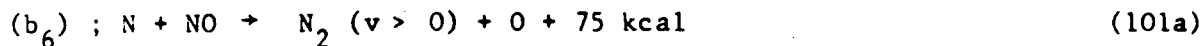
$$A = \frac{a_5 n(OH) + a_7 n(HO_2) + 2b_3 n(NO_2)}{2k_3 n(O_3)} \quad (100)$$

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



must have its major action above the ozone peak where there 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



with a relatively high rate coefficient at 300 K [Phillips and Schiff, 1962]

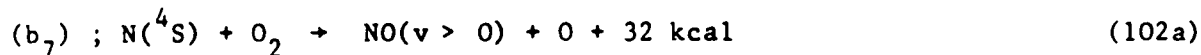
$$b_6 = 2.2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} . \quad (101b)$$

Between 298 and 670 K, the rate coefficient is given by the expression

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

according to Clyne and Mc Bernid (1975). Such a reaction is not important in the stratosphere, except in the case of exceptional (artificial) disturbances when atomic nitrogen is produced.

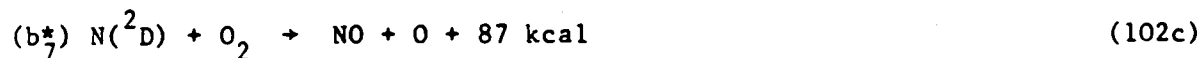
The reaction of atomic nitrogen with molecular oxygen is the general process to produce nitric oxide. A normal atom $N(^4S)$ leads to



which has a high activation energy. The last laboratory measurement (Becker et al., 1969) results in

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

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

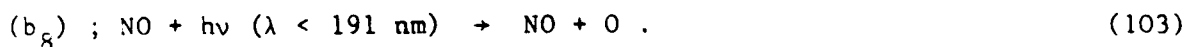


leads to an average value of the order of

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

according to measurements made by Lin and Kaufman (1971), Slanger et al. (1971) and Husain et al. (1972).

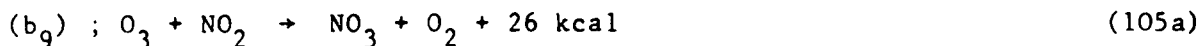
In addition to the loss process of nitric oxide (b_6) which occurs only when atomic nitrogen is sufficiently abundant, it is necessary to consider the photodissociation process which occurs in the mesosphere but which can also play a role in the upper stratosphere (Cieslik and Nicolet, 1973)



Thus, the photoequilibrium conditions between N and NO can be defined by reactions b_6 , b_7 and b_8

$$n(\text{O}_2) [b_7 n(\text{N}) + b_7^* n(\text{N}^*)] = n(\text{NO}) [J_{\text{NO}} + b_6 n(\text{N})] . \quad (104)$$

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

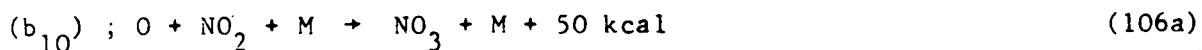


which leads to the production of nitrogen trioxide must be introduced.

Various recent laboratory measurements (Johnson and Graham, 1974 ; Huie and Herron, 1974 ; Davis et al., 1974a) give $(6.1 \pm 0.1) \times 10^{-19}$ at 200°K corresponding to the average value

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

Also, the three-body reaction



may occur in the region where atomic oxygen is present. Its rate coefficient (Gaedtke and Troe, 1975 ; Hippler et al., 1974) is

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

and

$$b_{10M_{\text{no}}} = 2.0 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} . \quad (106c)$$

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



for which (Harker and Johnston, 1973; Glänzer and Troe, 1973) the following rate coefficient can be adopted, (T = 297 K),

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

In addition there are two possible photodissociation processes



and



The photodissociation of $\text{NO}_3 + \text{NO} + \text{O}_2$ was adopted for several years by various authors (Crutzen, 1973; 1974; Levy, 1973; etc) following Johnston (1974). However, a recent communication by H.S. Johnston (1975, not yet published) indicates that the photodissociation should be $\text{NO}_3 + \text{NO}_2 + \text{O}$ and not process (109). Such a result is important since it indicates that the night-time process (b_9) of formation of nitrogen trioxide is counterbalanced by its day-time photodissociation. The destruction process of ozone in the lower stratosphere which was considered as follows :

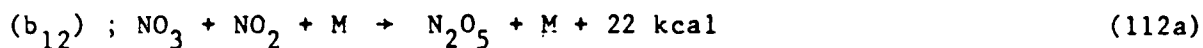


must be replaced by



where (110a) and (110b) are associated.

Nevertheless, there are other reactions involving NO_2 particularly for night-time conditions in the lower stratosphere. The following processes can be considered



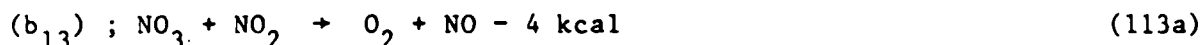
with the rate coefficients (see Baulch et al., 1973)

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

and

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

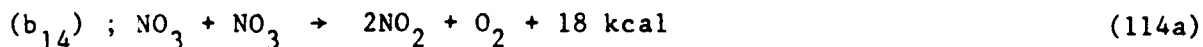
which is reached at about 20 km. The endothermic reaction



would have a rate coefficient (Baulch et al., 1973)

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

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

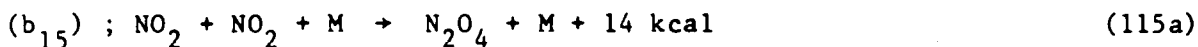


requires a high activation energy for stratospheric values. A suggested value of the rate coefficient (Baulch et al., 1973) is

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

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

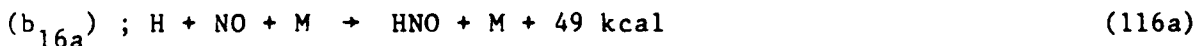
From this analysis of the various reactions of nitrogen trioxide, it is not clear if NO_3 can play a major role in stratospheric aeronomy. Its nighttime formation (reaction b_9) is always compensated for by daytime destruction processes. However, the action of nitroxyl, nitrous acid and nitric acid must 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 nighttime conditions

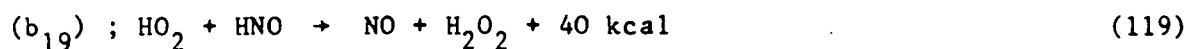
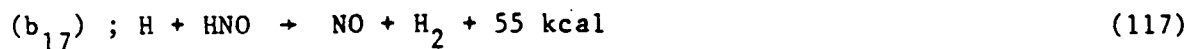


for which the rate coefficient is small (Clyne and Thrush, 1962),

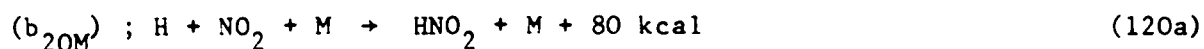
$$b_{15} = 8 \times 10^{-34} n(\text{M}) \text{ cm}^3 \text{ sec}^{-1} . \quad (115b)$$

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

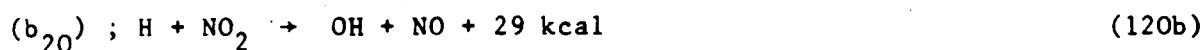




We consider now (Nicolet, 1965a) the various possible reactions leading to nitrous and nitric acids. We begin with the three-body association



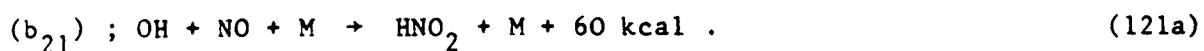
which is negligible in comparison with



where (Clyne and Monkhouse, private communication, 1975),

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

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



Measurements by Morley and Smith (1972) and Anderson et al. (1974) lead to the same result

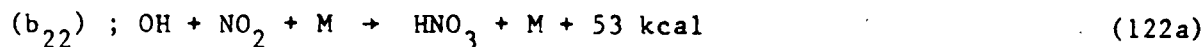
$$b_{21M} = 3.25 \times 10^{-32} e^{850/T} n(M) \text{ cm}^3 \text{ sec}^{-1} \quad (121b)$$

with the possible limit (Sie et al., 1975b)

$$b_{21M_{\infty}} = 1.2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} . \quad (121c)$$

when the value a_{36M^∞} (eq. 56c) is used for comparison.

The reaction of OH with NO_2 , which leads to nitric acid, is also extremely important :



with (Anderson et al., 1974)

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

and, at room temperature,

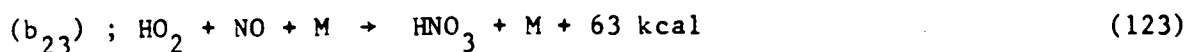
$$b_{22M^\infty} = 1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} . \quad (122c)$$

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^∞} 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 $n(\text{N}_2)$ varying from $1.6 \times 10^{19} \text{ cm}^{-3}$ to $3.2 \times 10^{17} \text{ cm}^{-3}$ between 220 K 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 following average values are obtained for the standard U.S. atmospheres at latitudes $\varphi = 15^\circ$ and $\varphi = 45^\circ$, respectively, (with an efficiency $n(\text{N}_2)/n(\text{O}_2) = 3/2$)

Altitude (km)	$\varphi = 45^\circ$	$\varphi = 15^\circ$
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}

The reaction involving HO_2 has not yet been observed,

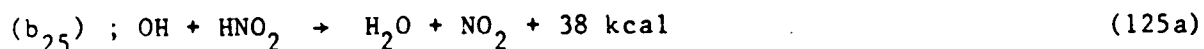


and may be neglected.

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



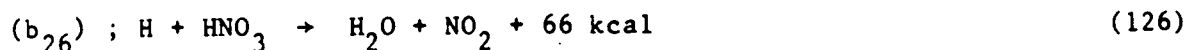
is not important compared with



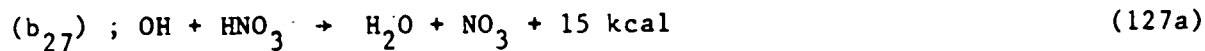
where

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

according to Cox (1974b). The reaction of H with HNO_3



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

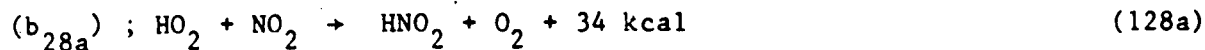


where

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

according to the most recent measurement (Zellner and Smith, 1974 ; Smith and Zellner, 1975).

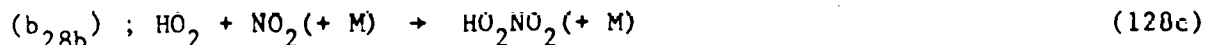
Another reaction which should be introduced (Simonaitis and Heicklen, 1974a; Cox and Derwent, 1975)



with a reported rate coefficient

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

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 as the following



leading perhaps to a long lived complex at stratospheric temperatures. The important reaction



which was introduced in the determination of the ratio $n(\text{OH})/n(\text{HO}_2)$ in the lower stratosphere, (eq. 57), has a rate coefficient which is still not known with precision. Davis et al. (1973c) and Payne et al. (1973) give

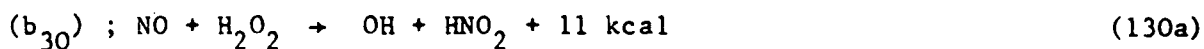
$$b_{29} = 3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (129b)$$

with a stated uncertainty of a factor 3. Hack et al. (1975) give

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

whereas Simonaitis and Heicklen (1975c) find $b_{29} = (1.0 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 300 K based on $a_{27} = 3.3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ and Cox and Derwent (1975) obtain $b_{29} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 296 K.

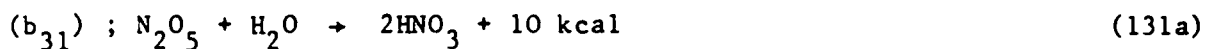
The reactions of hydrogen peroxide with nitrogen dioxide and nitric oxide are too slow to play a role in the stratosphere. According to Gray et al. (1972)



has a rate coefficient

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

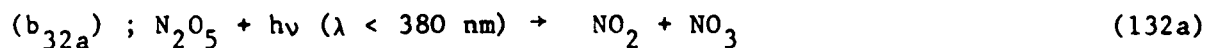
With the formation of dinitrogen pentoxide (reaction b_{12}) it is necessary to introduce the reaction with H_2O which is often considered. According to Morris and Niki (1973)



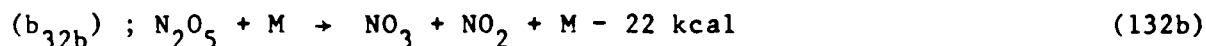
would have a rate coefficient at 250 K

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

However, the photodissociation must be considered



and the dissociation by collision



where (Baulch et al., 1973 ; Niki, 1974)

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

or

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

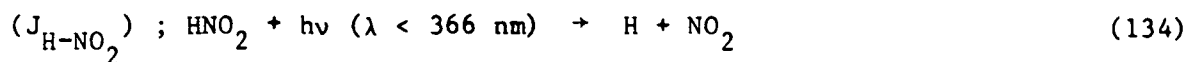
at 1 atm and 297 K (Harker and Johnston, 1973).

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

The primary products of HNO_2 photodissociation are



and



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, 1974a)



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_2O_5 , NO_3 , HNO_2 and NO_2 since their photodissociations are sufficiently rapid. We may write for N_2O_5 , NO_3 , HNO_2 and NO_2 , respectively

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

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

$$n(\text{NO}_2) [b_9 n(\text{O}_3) + b_{10} n(\text{M}) n(\text{O})] + b_{27} n(\text{OH}) n(\text{HNO}_3) + b_{32} n(\text{N}_2\text{O}_5) \quad (137)$$

$$n(\text{HNO}_2) [J_{\text{OH-NO}} + J_{\text{H-NO}_2} + b_{25} n(\text{OH})] = b_{21} n(\text{M}) n(\text{NO}) n(\text{OH}) + b_{28} n(\text{NO}_2)$$

$$n(\text{HO}_2) \quad (138)$$

$$n(\text{NO}_2) [J_{\text{NO}_2} + b_3 n(\text{O}) + b_9 n(\text{O}_3) + b_{10} n(\text{M}) n(\text{O}) + b_{12} n(\text{M}) n(\text{NO}_3) +$$

$$+ b_{22} n(\text{M}) n(\text{OH}) + b_{28} n(\text{HO}_2)] =$$

$$n(\text{NO}) [b_2 n(\text{M}) n(\text{O}) + b_4 n(\text{O}_3) + 2b_{11} n(\text{NO}_3) +$$

$$b_{29} n(\text{HO}_2) + c_{5a} n(\text{CH}_3\text{O}_2)] + n(\text{HNO}_2) [J_{\text{H-NO}_2} + b_{25} n(\text{OH})]$$

$$+ n(\text{HNO}_3) J_{\text{OH-NO}_2} + n(\text{NO}_3) J_{\text{NO}_2-\text{O}} \quad (139)$$

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

$$n(\text{N}) [b_1 n(\text{M}) n(\text{O}) + b_6 n(\text{NO}) + b_7 n(\text{O}_2)] = n(\text{NO}) J_{\text{NO}} + P(\text{N}) \quad (140)$$

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_{36} involving all hydrogen reactions, the equations governing the rates of change of the concentration of ozone and atomic oxygen become

$$\frac{dn(O_3)}{dt} + n(O_3) [J_3 + k_3 n(O) + a_2 n(H) + a_6 n(OH) + a_{6c} n(HO_2) + b_4 n(NO) + b_9 n(NO_2)] = k_2 n(M) n(O_2) n(O) \quad (141)$$

$$\begin{aligned} \frac{dn(O)}{dt} + n(O) [2k_1 n(M) n(O) + k_2 n(M) n(O_2) + k_3 n(O_3) + a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + b_1 n(M) n(N) + \\ b_2 n(M) n(NO) + b_3 n(NO_2) + b_{10} n(M) n(NO_2)] = \\ 2n(O_2) J_2 + n(O_3) J_3 + n(NO) J_{NO} + n(NO_2) J_{NO_2} + n(NO_3) J_{NO_2-O} \\ + n(N) [b_6 n(NO) + b_7 n(O_2)] . \end{aligned} \quad (142)$$

Since atomic oxygen (eq. 142) and atomic nitrogen (eq. 140) are always in photochemical equilibrium in the stratosphere, the ozone equation (141) becomes, ($a_2 n(H)$ and $2k_1 n(O)$ being neglected),

$$\begin{aligned} \frac{dn(O_3)}{dt} + n(O_3) [2k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2) + b_4 n(NO) + b_9 n(NO_2)] \\ + n(O) [a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + 2b_1 n(M) n(N) \\ + b_2 n(M) n(NO) + \{ b_3 + b_{10} n(M) \} n(NO_2)] = \\ 2n(O_2) J_2 + 2n(NO) J_{NO} + P(N) + n(NO_2) J_{NO_2} + n(NO_3) J_{NO_2-O} . \end{aligned} \quad (143)$$

Thus the addition of nitrogen oxides NO and NO₂ which destroy odd oxygen by various reactions involving ozone and atomic oxygen must be considered with its counterpart, the photodissociation of NO, NO₃ and NO₂ and of 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 the 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):

$$\begin{aligned} \frac{dn(O_3)}{dt} + n(O_3) [2k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2)] \\ + n(O) [a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + 2b_3 n(NO_2)] = \\ - n(NO_2) [b_{22} n(M) n(OH) + b_{28} n(HO_2)] - 2k_{31} n(H_2O) n(N_2O_5) \\ + 2n(O_2) J_2 + n(NO) [2 J_{NO} + b_{29} n(HO_2) + c_{5a} n(CH_3O_2)] + P(N) \\ + n(HNO_3) [J_{OH-NO_2} + b_{27} n(OH)] + n(HNO_2) [J_{H-NO_2} + b_{25} n(OH)]. \quad (144) \end{aligned}$$

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

$$\begin{aligned} \frac{dn(HNO_3)}{dt} + n(HNO_3) [J_{OH-NO_2} + b_{27} n(OH)] = b_{22} n(M) n(OH) + n(NO_2) \\ + 2b_{31} n(H_2O) n(N_2O_5) \quad (145) \end{aligned}$$

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

$$\begin{aligned}
& \frac{dn(O_3)}{dt} + n(O_3) [2k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2)] \\
& + n(O) [a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + 2b_3 n(NO_2)] \\
& = 2n(O_2) J_2 + n(NO) [2 J_{NO} + c_{5a} n(CH_4O_2)] + P(N) + n(HNO_2) J_{H-NO_3} \\
& + n(OH) [b_{25} n(HNO_2) + b_{27} n(HNO_3)] \\
& + n(HO_2) [b_{29} n(NO) - b_{28} n(NO_2)] \\
& = 2n(O_2) J_2 + n(NO) [2 J_{NO} + b_{21} n(M) n(OH) + b_{29} n(HO_2) \\
& + c_{5a} n(CH_3O_2)] + P(N) + n(HNO_3) b_{27} n(OH) - n(HNO_2) J_{OH-NO} . \quad (146)
\end{aligned}$$

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

$$n(O) = \frac{n(O_3) J_3 + n(NO_2) J_{NO_2}}{k_2 n(M) n(O_2)} , \quad (147)$$

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

$$\begin{aligned}
& \frac{dn(O_3)}{dt} + \frac{2 k_3 J_3}{k_2 n(M) n(O_2)} n^2(O_3) \left[1 + \frac{n(NO_2) J_{NO_2}}{n(O_3) J_3} \right] + \\
& n(O_3) \left\{ [a_6 n(OH) + a_{6c} n(HO_2)] + \frac{J_3}{k_2 n(M) n(O_2)} \left[1 + \frac{n(NO_2) J_{NO_2}}{n(O_3) J_3} \right] \right\} \\
& [a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + 2b_3 n(NO_2)] \} =
\end{aligned}$$

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 in the stratosphere. In particular, the following term

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

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 eq. (88) and (90)], is given, with the effect of nitrogen oxides, by

$$\begin{aligned} n(HO_2) [a_{6c} n(O_3) + a_7 n(O) + a_{17} n(OH) + 2a_{27} n(HO_2) + b_{29} n(NO) + \\ b_{28} n(NO_2)] = n(OH) [a_5 n(O) + a_6 n(O_3) + a_{19} n(H_2) \\ + a_{30} n(H_2O_2) + a_{36} n(CO) + c_8 n(H_2CO) + c_2 Xn(CH_4)] \quad (152a) \end{aligned}$$

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

$$\begin{aligned} n(HO_2) [a_{6c} n(O_3) + a_7 n(O) + b_{29} n(NO)] = n(OH) [a_5 n(O) + a_6 n(O_3) \\ + a_{36} n(CO)] . \quad (152b) \end{aligned}$$

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

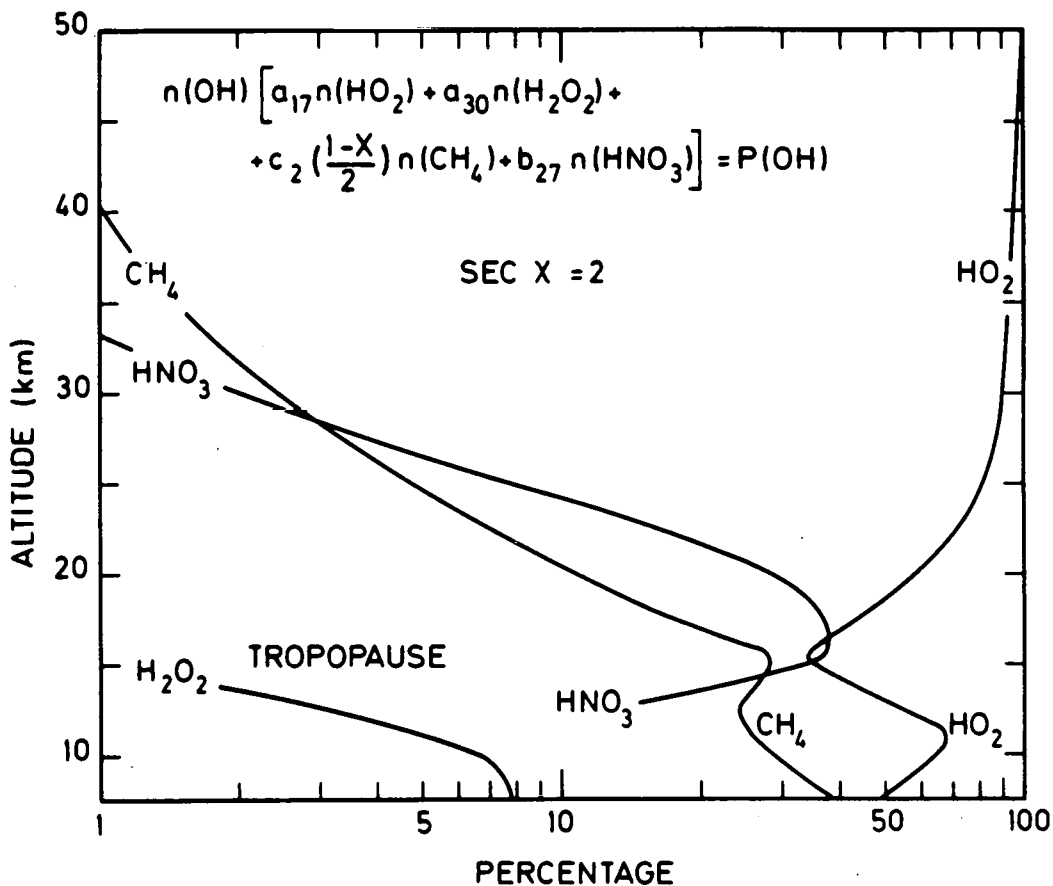


Fig. 9.- Example of possible profiles (%) of various terms determining the concentration of hydroxyl radical, using profiles of figures 5 and 6. The effect of CH₄ corresponds to a certain value X which was obtained in 1973 for the photodissociation of formaldehyde H₂ + CO and H + COH, and such an effect is very sensitive to the value of X used.

$$n(\text{OH}) [n(\text{HO}_2) a_{17} + n(\text{HNO}_3) b_{27}] =$$

$$a^* n(\text{O}^*) [n(\text{H}_2\text{O}) + n(\text{H}_2) + \frac{1+X}{2} n(\text{CH}_4)] + c_2 \left(\frac{X-1}{2}\right) n(\text{CH}_4) n(\text{OH}) \quad (153)$$

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

Figure 9 shows (Nicolet, 1974) the importance of the reaction (a_{17}) $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ if the rate coefficient reaches $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. 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 :

$$\frac{dn(\text{NO})}{dt} + n(\text{NO}) [J_{\text{NO}} + b_2 n(\text{M}) n(\text{O}) + b_6 n(\text{N}) + b_4 n(\text{O}_3) +$$

$$b_{11} n(\text{NO}_3) + b_{21} n(\text{M}) n(\text{OH}) + b_{29} n(\text{HO}_2) + c_{5a} n(\text{CH}_3\text{O}_2)]$$

$$= b_1 n(\text{M}) n(\text{O}) n(\text{N}) + 2b_5 n(\text{N}) n(\text{NO}_2) + b_7 n(\text{N}) n(\text{O}_2) +$$

$$n(\text{NO}_2) J_{\text{NO}_2} + b_3 n(\text{O}) n(\text{NO}_2) + n(\text{HNO}_2) J_{\text{OH-NO}} + P(\text{NO}) \quad (154)$$

where $P(\text{NO})$ is the direct production of nitric oxide molecules.

By combining all equilibrium equations involving N_2O_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 :

$$\frac{dn(\text{NO})}{dt} + \frac{dn(\text{HNO}_3)}{dt} = P(\text{N}) + P(\text{NO}) - 2 b_6 n(\text{N}) n(\text{NO}) \quad (155a)$$

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

$$\frac{dn(\text{NO})}{dt} + \frac{dn(\text{HNO}_3)}{dt} + 2b_6 J_{\text{NO}} \frac{n^2(\text{NO})}{b_6 n(\text{NO}) + b_7 n(\text{O}_2)} =$$

$$\frac{b_7 n(\text{O}_2) - b_6 n(\text{NO})}{b_7 n(\text{O}_2) + b_6 n(\text{NO})} P(\text{N}) + P(\text{NO}) \quad (155b)$$

$$\text{where } b_7 n(\text{O}_2) > b_6 n(\text{NO}) . \quad (155c)$$

Let us use the ratio

$$\frac{n(\text{NO}_y)}{n(\text{NO})} = R \quad (156a)$$

$$\text{where } n(\text{NO}_y) = n(\text{HNO}_3) + n(\text{NO}) \quad (156b)$$

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

$$\frac{\partial n(\text{NO}_y)}{\partial t} + 2b_6 J_{\text{NO}} \frac{n^2(\text{NO}_y)}{[b_6 n(\text{NO}_y) + R b_7 n(\text{O}_2)]} + \text{div } \phi(\text{NO}_y)$$

$$\frac{R b_7 n(\text{O}_2) - b_6 n(\text{NO}_y)}{R b_7 n(\text{O}_2) + b_6 n(\text{NO}_y)} P(\text{N}) + P(\text{NO}) \quad (157)$$

if the control by eddy diffusion transport is introduced.

Taking into account condition (155c) and considering that the production $P(\text{N})$ is compensated by the rapid transformation of N in NO under normal conditions, the following equation pertaining to the variation of

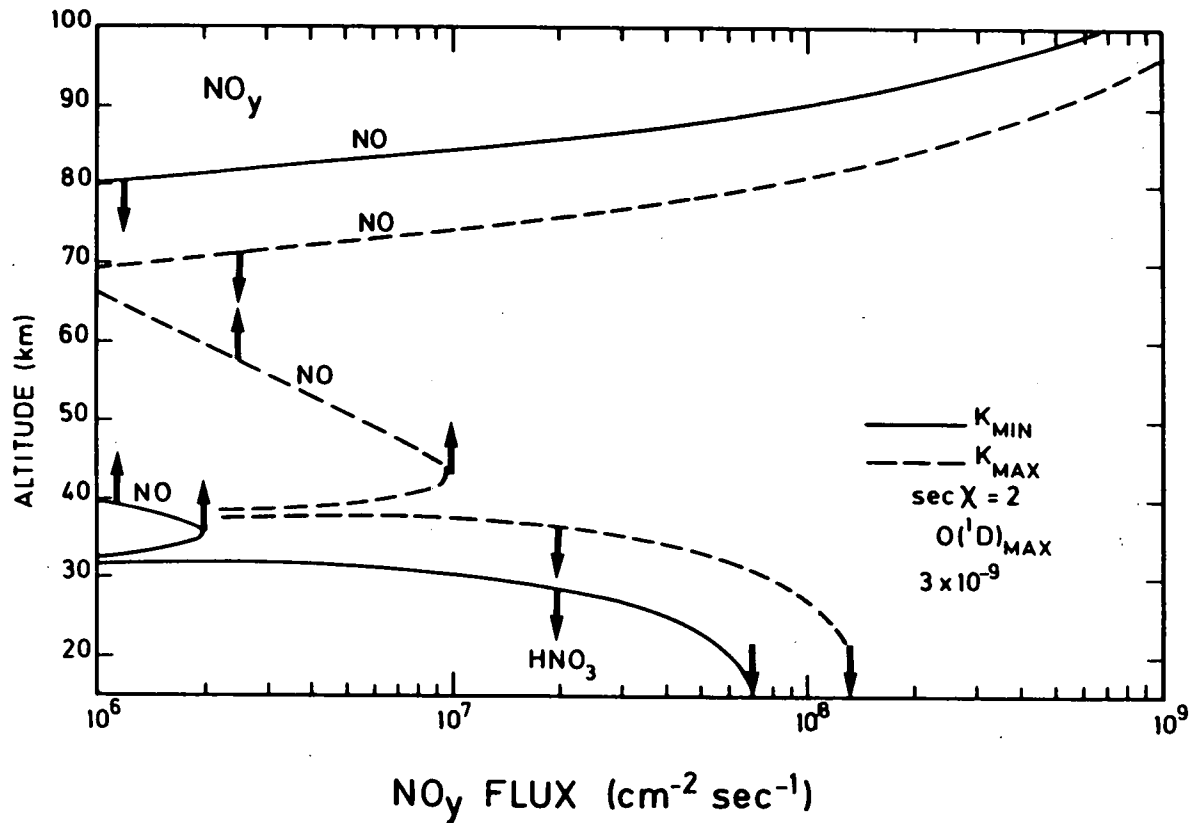


Fig. 10.- Examples of vertical transport of NO and HNO₃ for arbitrary conditions of eddy diffusion coefficients K_{max} and K_{min} and upper and lower boundary conditions at 100 km and at 15 km; upward and downward currents are shown by NO at the stratopause and by HNO₃ at the tropopause, respectively.

NO_y can be written as follows at the stratopause level, ($\text{NO}_y = \text{NO}$ and $J_{\text{NO}} \neq 0$),

$$\frac{\partial n(\text{NO})}{\partial t} + \frac{2 b_6 J_{\text{NO}}}{b_7 n(\text{O}_2)} n^2(\text{NO}) + \text{div } \phi(\text{NO}) = P(\text{NO}) \quad (158a)$$

and in the lower stratosphere

$$\frac{\partial n(\text{NO}_y)}{\partial t} + \text{div } \phi(\text{NO}_y) = P(\text{NO}) \quad (158b)$$

since $J_{\text{NO}} = 0$; 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.

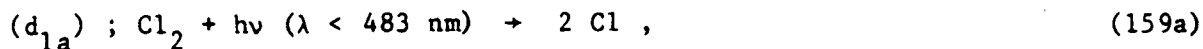
Thus, the nitrogen oxide concentrations, and particularly those of HNO_3 , NO and NO_2 , must depend on atmospheric conditions in the lower stratosphere (see Fig. 10; Brasseur and Nicolet, 1973) and their behavior will be related to the variation of the tropopause. The action of the advection and various 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 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 $n(\text{OH})/n(\text{HO}_2)$ is related to $n(\text{NO})$ and $n(\text{CO})$ in the lower stratosphere while $n(\text{HNO}_3)$ depends on $n(\text{OH})$ and $n(\text{OH})$ is not independent of $n(\text{HNO}_3)$.

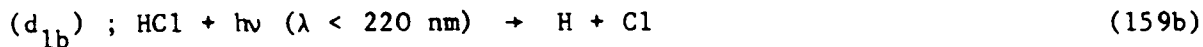
7. REACTIONS IN A CHLORINE-NITROGEN-HYDROGEN-OXYGEN ATMOSPHERE

As was mentioned in the introduction, the role of chlorine compounds as catalyst 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 , and of the dichlorofluoromethane, CF_2Cl_2 , which are observed in the troposphere (CFCl_3 , Lovelock, 1971, 1972; Lovelock *et al.*, 1973; Wilkniss *et al.*, 1973; Lovelock, 1974; Wilkniss *et al.*, 1975a; CFCl_3 and CF_2Cl_2 , Su and Goldberg, 1973). The action of Freon production (McCarthy, 1974; McCarthy and Jesson, unpublished, 1975) on stratospheric ozone has been analyzed in different ways by several authors (Rowland and Molina, 1975; Crutzen, 1974b; Cicerone *et al.*, 1974; 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; Murray and Riley, 1973; Su and Goldberg, 1973; Wilkniss *et al.*, 1973; Lovelock, 1975; Simmonds *et al.*, 1974; Wilkniss *et al.*, 1975b), 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).

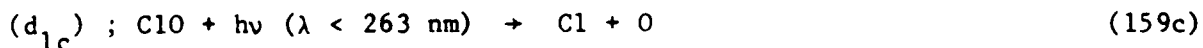
The problem of chlorine species in the stratosphere begins, after their transport from the troposphere, by their photodissociation in the ozonosphere. Among the various dissociation processes, we may consider the following :



is photodissociated in the stratosphere and troposphere by radiation of $\lambda > 300 \text{ nm}$ (Seery and Britton, 1964) and cannot be an important minor constituent.

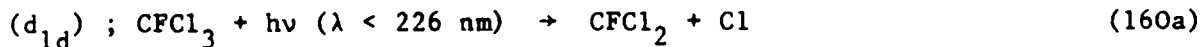


is photodissociated for wavelength shorter than 300 nm. Laboratory measurements (Romand, 1949; Myer and Samson, 1970) which have been made between λ 207 nm and 139 nm indicate that the dissociation of hydrogen chloride can only occur in the stratosphere.



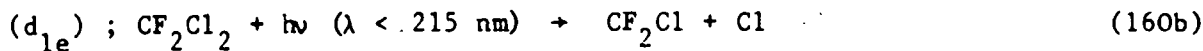
The continuous absorption occurs beyond 263 nm (Durie and Ramsay, 1958), but there is a predissociation at 290 nm in the (7-0) band. The total photodissociation is, therefore, not easy to determine. With the cross-sections as given by Johnston et al. (1969), it may be concluded that the ClO photodissociation 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), and the dominant photochemical process is



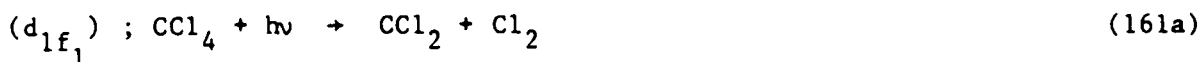
for which laboratory measurements (Marsh and Heicklen, 1965; Jayanty et al., 1975b) indicate that the quantum yield is unity.

For CF_2Cl_2 , very recent results by Milstein and Rowland (1975) and Jayanty et al. (1975b), after determination of the absorption cross sections (Rowland and Molina, 1975), indicate that



for which the quantum yield is unity for the photooxidation by 184.9 nm and 213.9 nm photolysis in the presence of O_2 . Thus both CFCl_3 and CF_2Cl_2 absorb solar radiation in the stratosphere and cannot be photolysed in the troposphere.

The photodissociation of carbon tetrachloride occurs also in the stratosphere, according to the absorption cross-sections 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 pressures, according to Jayanty et al. (1975a)



and at high pressures the process

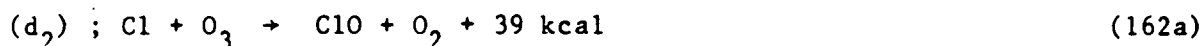


may occur.

Other fluorocarbons should be also 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 1975) shows that the photochemical behavior in the stratosphere of the various fluorocarbons depends on the number of chlorine (and bromine) atoms. Molecules like CH_3Cl (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_2Cl_2 , CCl_4 , etc. 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

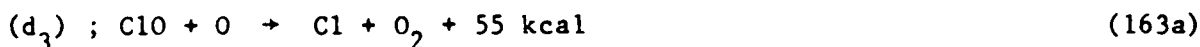


with a rate coefficient, (Davis, private communication, 1975)

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

in the temperature range 220-298 K; which leads to $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ in the upper stratosphere i.e. about a factor of two less than the first value given by Clyne and Watson at room temperature. A very precise value of the rate coefficient of such a reaction is required since it could play a leading role in the upper stratosphere.

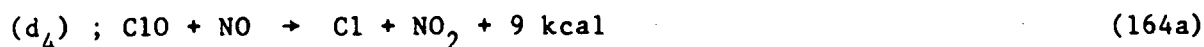
The ClO radical is subject to two rapid bimolecular reactions in the stratosphere



with a reported rate coefficient, (Bemand et al., 1973),

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

and

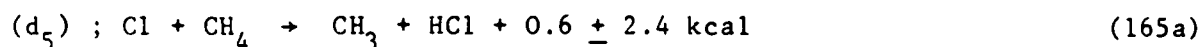


with a rate coefficient, (Clyne and Watson, 1974),

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

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_2O_2 and HNO_3 .

The first reaction which has been considered (Rowland and Molina, 1974a; Stolarski and Cicerone, 1974; Wofsy and McElroy, 1974) is

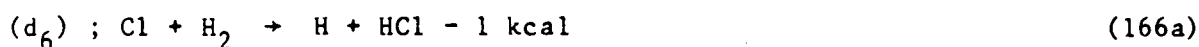


for which the rate coefficient has been measured between 218 and 350 K by Davis et al. (1975) (Davis, private communication)

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

leading to $1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at 300 K and to $2 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at 200 K.

The reaction with molecular hydrogen

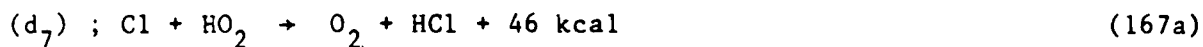


leads to $d_6 = 1.4 \times 10^{-14}$ at 298 K (Davis et al., 1970). After the preliminary values of Clyne and Walker (1973) the following rate coefficient (Davis, private communication, 1975) should be adopted

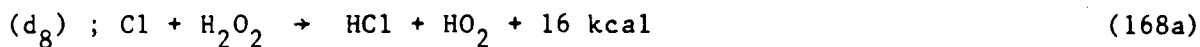
$$d_6 = 5.7 \times 10^{-11} e^{-2400/T} \text{ cm}^3 \text{ sec}^{-1} ; \quad (166b)$$

it leads to $1.8 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ at 298 K and $3.5 \times 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$ at 200 K.

No laboratory measurements have been made for the reaction of Cl with HO₂, H₂O₂ and HNO₃ and values that have been used (Wofsy and McElroy, 1974; Crutzen, 1974b; Molina and Rowland, 1975) are estimates obtained by comparison with other reactions



$$\text{with } d_7 = 1 \times 10^{-11} \text{ to } 10^{-10} \text{ cm}^3 \text{ sec}^{-1} . \quad (167b)$$

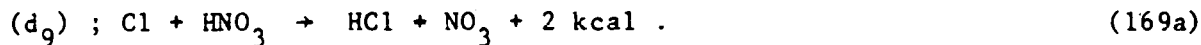


with the value of the rate coefficient assumed to be (Molina and Rowland, 1975),

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

i.e. ten times the rate coefficient of OH with H₂O₂.

In addition



also with the value of the rate coefficient assumed to be (Molina and Rowland, 1975),

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

i.e. ten times the rate coefficient of OH with HNO₃ .

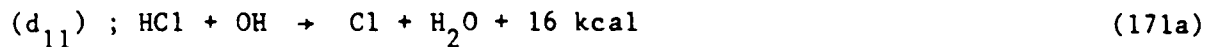
Hydrogen chloride molecules which are formed by all the preceding reactions (165) to (169) but particularly by Cl + CH₄ may react in a bimolecular process such as



with a rate coefficient (Brown and Smith, 1975) of

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

The other reaction which plays a role at stratospheric level is



for which there are excellent laboratory measurements over a large range of temperatures (213 to 478 K) by Smith and Zellner (1974) and Zahnizer et al. (1974) leading to an average value

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

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

$$n(\text{ClO}) [J_{\text{ClO}} + d_3 n(\text{O}) + d_4 n(\text{NO})] = d_2 n(\text{Cl}) n(\text{O}_3) \quad (172)$$

since $dn(\text{ClO})/dt = 0$ in stratospheric conditions where $d_3 n(\text{O}) + d_4 n(\text{NO}) > 10^{-3} \text{ sec}^{-1}$. It is, therefore, possible to deduce the ratio $n(\text{ClO})/n(\text{Cl})$ and to determine the concentration of chlorine atoms by

$$\begin{aligned} n(\text{Cl}) [d_2 n(\text{O}_3) + d_5 n(\text{CH}_4) + d_6 n(\text{H}_2) + d_7 n(\text{HO}_2) + d_8 n(\text{H}_2\text{O}_2) \\ + d_9 n(\text{HNO}_3)] = n(\text{HCl}) [J_{\text{HCl}} + d_{10} n(\text{O}) + d_{11} n(\text{OH})] \\ + n(\text{Cl}_2) J_{\text{Cl}_2} + n(\text{ClO}) J_{\text{ClO}} + n(\text{CFCl}_3) J_{\text{CFCl}_3} + n(\text{CF}_2\text{Cl}_2) J_{\text{CF}_2\text{Cl}_2} + \\ n(\text{CCl}_4) J_{\text{CCl}_4} + \dots \end{aligned} \quad (173)$$

since $d_2 n(O_3) > 10^{-1} \text{ sec}^{-1}$ in the stratosphere. Thus the practical equation for the determination of the Cl concentration is

$$n(\text{Cl}) d_2 n(O_3) = P(\text{Cl}) \quad (174)$$

where $P(\text{Cl})$ 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 $n(\text{HCl})$ is

$$\frac{dn(\text{HCl})}{dt} + n(\text{HCl}) [J_{\text{HCl}} + d_{10} n(\text{O}) + d_{11} n(\text{OH})] = n(\text{Cl}) [d_5 n(\text{CH}_4) + d_6 n(\text{H}_2) + d_7 n(\text{HO}_2) + d_8 n(\text{H}_2\text{O}_2) + d_9 n(\text{HNO}_3)] \quad (175)$$

It is not possible to write conditions for the day equilibrium since all terms J_{HCl} , $d_{10} n(\text{O})$ and $d_{11} n(\text{OH})$ 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

$$\frac{\partial n(\text{HCl})}{\partial t} + \text{div} [n(\text{HCl}) w(\text{HCl})] + n(\text{HCl}) [J_{\text{HCl}} + d_{10} n(\text{O}) + d_{11} n(\text{OH})] = n(\text{Cl}) [d_5 n(\text{CH}_4) + d_6 n(\text{H}_2) + d_7 n(\text{HO}_2) + d_8 n(\text{H}_2\text{O}_2) + d_9 n(\text{HNO}_3)] \quad (176)$$

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

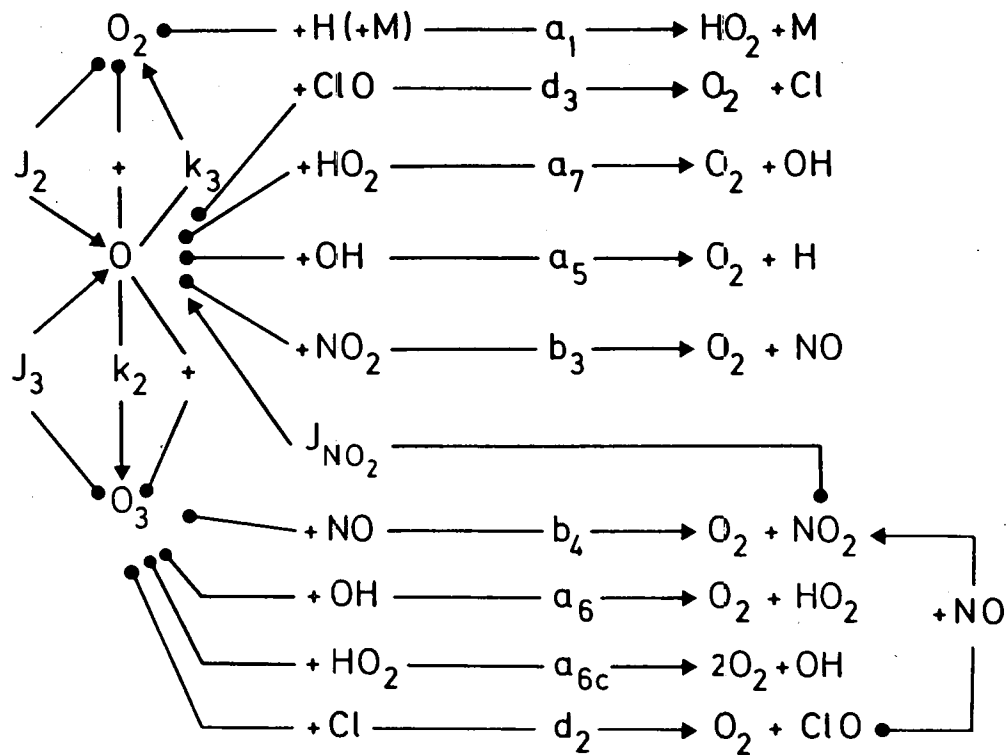


Fig. 11.- General reaction scheme in which are simultaneously involved the chlorine, nitrogen and hydrogen radicals (atoms or molecules) related directly to the production and loss of odd oxygen in the stratosphere.

from the tropopause of less than 10^{-10} to about 4×10^{-10} above 25 km.

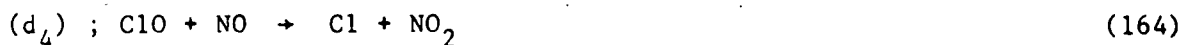
The catalytic removal of ozone by chlorine compounds occurs by the simultaneous action of



and



which is counterbalanced at lower levels by



Thus, the additional terms to be added to the general equation governing the rate of the concentration $n(\text{O}_3)$ in the stratosphere are

$$\begin{aligned} \frac{\partial n(\text{O}_3)}{\partial t} + \text{div} [n(\text{O}_3) w(\text{O}_3)] + \dots + n(\text{O}_3) d_2 n(\text{Cl}) + n(\text{O}) d_3 n(\text{ClO}) \\ = P(\text{O}) \end{aligned} \quad (177)$$

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

$$\begin{aligned} \frac{\partial n(\text{O}_3)}{\partial t} + \text{div} [n(\text{O}_3) w(\text{O}_3)] + \dots + 2n(\text{O}_3) d_2 n(\text{Cl}) = \\ P(\text{O}) + n(\text{ClO}) [J_{\text{ClO}} + d_4 n(\text{NO})] \end{aligned} \quad (178)$$

The form shown in (178) and illustrated in Fig. 11 indicates how chlorine atoms lead to the removal of stratospheric ozone. A concentration of chlorine atoms of the order of 5×10^5 leads to a loss rate of

$2 \times 10^{-5} n(O_3) \text{ cm}^{-3} \text{ sec}^{-1}$. However, when the Cl concentration is reduced to less than 10^4 cm^{-3} , the lifetime of an ozone molecule is still of the order of a year. On the other hand, the production term $d_4 n(NO) n(ClO)$ 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 $10^6 \text{ cm}^{-3} \text{ sec}^{-1}$, 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_3 (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 precision. The concentrations of hydrogen and nitrogen compounds should be known at least within a factor of two, 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 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 $n(ClO) \geq 5 \times 10^8 \text{ cm}^{-3}$, it is possible to write

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

i.e. that the ratio $n(\text{NO}_2)/n(\text{NO})$, which is well defined in a nitrogen-oxygen stratosphere, may change in a chlorine-nitrogen-oxygen atmosphere indicating 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 :



with, at temperatures between 200 and 300 K (Clyne and Cox, 1968),

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

A calculation by Watson (1974) gives the variation with height of the reverse reaction



d_{12r} increases from $2 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$ in the lower stratosphere to about 10^{-15} at the stratopause level.

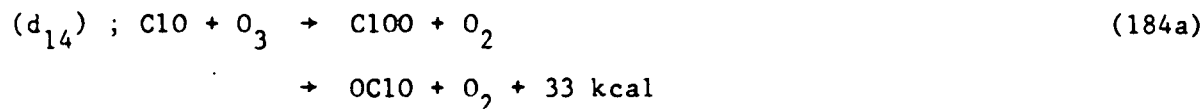
We may have also according to Simonaitis and Heicklen (1975b)



where at 300°K

$$d_{13} = (4 \pm 2) \times 10^{-30} n(\text{O}_2) \text{ cm}^3 \text{ sec}^{-1} . \quad (183b)$$

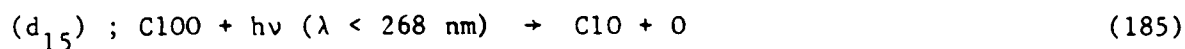
The reaction between ClO and O_3 leads to



where at 298 K (Davis et al., 1973)

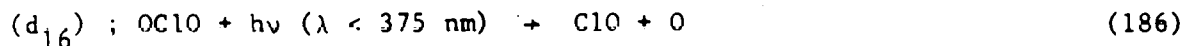
$$d_{14} \leq 5 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} . \quad (184b)$$

The photodissociation of ClO₀ occurs only at $\lambda < 300 \text{ nm}$



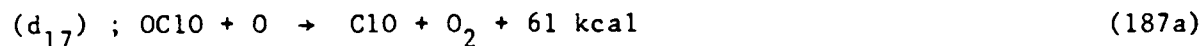
and can exist only in the stratosphere.

The photodissociation of ClO₁ at $\lambda > 300 \text{ nm}$



is related to a predissociation process that occurs at greater wavelengths than the dissociation continuum ($\lambda < 276 \text{ nm}$).

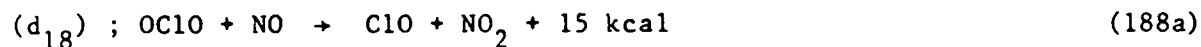
The reactions of ClO₁ with O and NO are as follows :



where (Bemand et al., 1973)

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

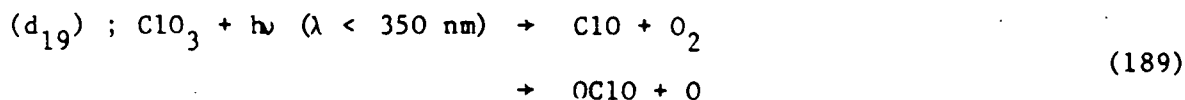
and



where (Bemand et al., 1973)

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

On the other hand, photodissociation of ClO₃ leads to ClO or ClO₁



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 :



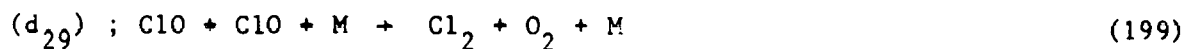
with a rate coefficient which could be of the order of

$$d_{20\infty} = 2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \tag{190b}$$

leading to a possible removal of stratospheric chlorine.

In addition to these reactions (182) to (190), which should be introduced for a discussion of compounds such as ClO_2 and ClO_3 , 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 :





Finally, reactions (Sandoval et al., 1974; Pitts et al., 1974; Jayanty et al., 1975a, b) such as



may be considered. Values of the rate coefficient d_{30} are of the order of $(3 + 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. 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 be also 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 $5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ if the OH concentration is of the order of $10^6 \text{ cm}^3 \text{ sec}^{-1}$ (daytime, ground level at 300 K). In the lower stratosphere the life time would be of the order of 5 years 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). 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 $\text{cm}^{-2} \text{sec}^{-1}$ with an upward flux of $1.7 \times 10^6 \text{cm}^{-2} \text{sec}^{-1}$ 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 - 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 year, according to Lovelock (1975), indicates that it is the most important stratospheric chlorine source which is produced by the biosphere.

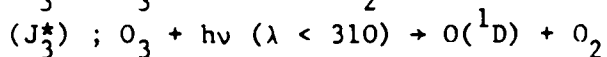
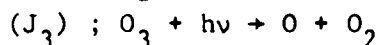
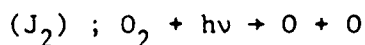
In conclusion, if the mixing ratio of odd chlorine tends to reach 10^{-9} , a very precise analysis is required since the efficiency for ozone depletion by the mechanism $d_2 \text{ n(Cl) n(O}_3) \text{ cm}^{-3} \text{ sec}^{-1}$ must be considered at the present time in the upper stratosphere (> 35 km) where the mechanism $d_4 \text{ n(ClO) n(NO) cm}^{-3} \text{ sec}^{-1}$ cannot counterbalance its effect as it can in the lower stratosphere (equation 172). A Cl concentration greater than $5 \times 10^4 \text{ cm}^{-3}$ and reaching 10^5 cm^{-3} would lead to ozone removal according the mechanism $2d_2 \text{ n(Cl) n(O}_3) \text{ cm}^{-3} \text{ sec}^{-1}$ which will compete with the mechanisms $2b_3 \text{ n(O) n(NO}_2)$ and $2a_5 \text{ n(O) n(OH)}$ 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 I 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 also noted that it is not sufficient to consider steady state conditions even involving transport in the lower stratosphere since tropopause variations are very important.

TABLE I.- Basic reactions involved in the determination of the ozone concentration in the stratosphere.

I. Oxygen atmosphere



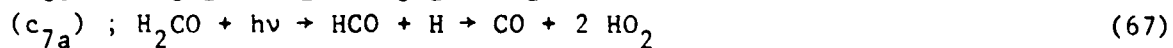
II. Hydrogen-oxygen atmosphere



In addition, for ratio $n(OH)/n(HO_2)$,



For production of OH



For loss of OH



III. Nitrogen-hydrogen-oxygen atmosphere.



In addition, for production and loss of nitrogen oxides,



IV. Chlorine-nitrogen-hydrogen-oxygen atmosphere.



Production and loss of HCl

8. 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 K but less than 6000 K. The solar constant is of the order of $1.95 \pm 0.01 \text{ cal cm}^{-2} \text{ min}^{-1}$ or $136 \pm 1 \text{ mW cm}^{-2}$ (Labs and Neckel, 1971; Thekaekara, 1973; Willson, 1973), which corresponds to an effective temperature of the order of $5770 \pm 10 \text{ K}$. This temperature is the absolute temperature T_S 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 :

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

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

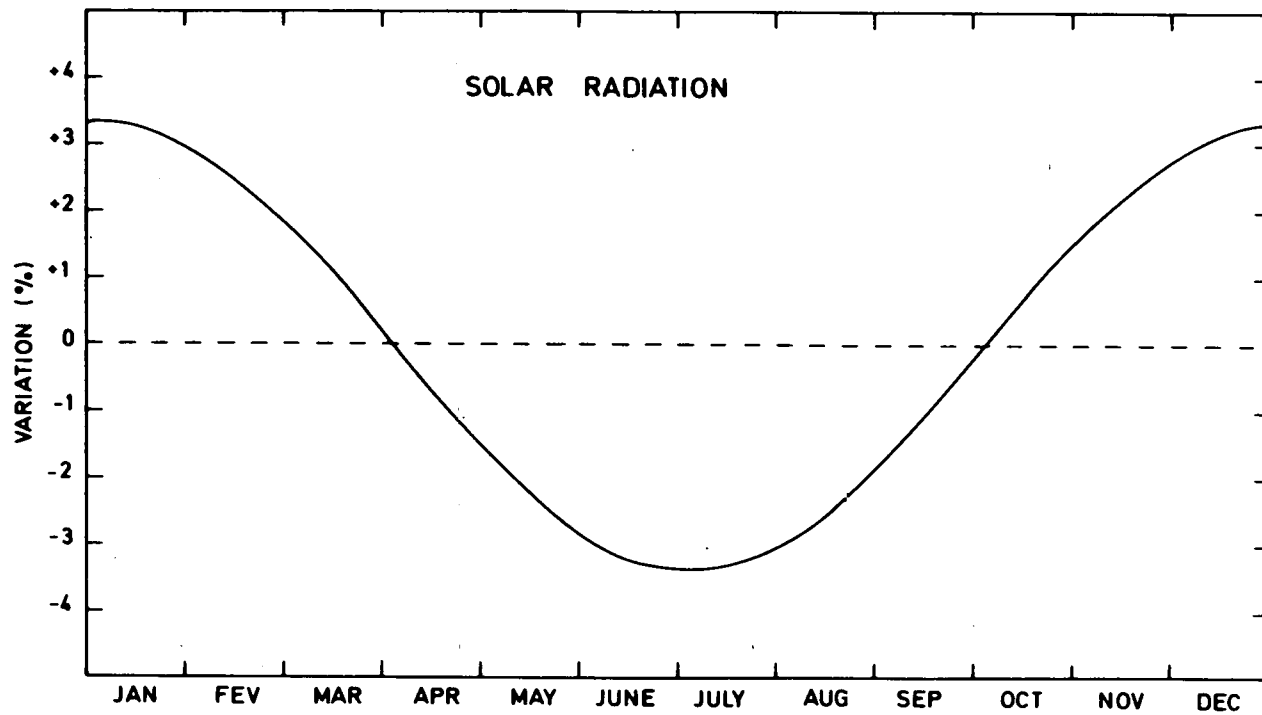


Fig. 12.- Variation (in percent) of the solar flux corresponding to the variation of the sun to earth distance ; variations are 6.6% between the first week of January and the first week of July.

At the top of the earth's atmosphere, the radiation density $\rho_S(\nu)$ is reduced by the dilution factor β_S

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

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 Fig. 12 and corresponds to \pm 3.3 percent. The maximum occurs in the first week of January and leads to

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

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

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

There is, therefore, a variation of 6.6 percent every six 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 percent 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 $2.01 \text{ cal cm}^{-2} \text{ min}^{-1}$ in January and to the minimum value of $1.88 \text{ cal cm}^{-2} \text{ min}^{-1}$ in July.

As we go down the wavelength scale from 290 nm to 250 nm the brightness temperature decreases from 5500 K to 5000 K (see 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 nm and 130 nm is $T = 4525 \pm 25$ 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 $\text{cm}^{-2} \text{sec}^{-1}$ available at the top of the terrestrial atmosphere. The number of photons of frequency ν , $q(\nu)$, is given, from (1), by

$$q(\nu) = \frac{c \beta_S \rho_S(\nu)}{h\nu} = \frac{8 \pi \beta_S \nu^2}{c^2} \left(e^{h\nu/kT} - 1 \right)^{-1} \quad (203)$$

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

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

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 $\nu_1 - \nu_2$,

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

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 $\text{cm}^{-2} \text{sec}^{-1}$ in the Schumann-Runge continuum which corresponds to a brightness temperature of 4900 K. A reduction of not less than 200K 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 $6.3 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ corresponding to a brightness temperature of only 4525 ± 25 K which must be introduced in aeronomic calculations.

In the spectral region of the Schumann-Runge bands (200 nm to 175 nm) the absolute values of the solar radiation flux are not well known. Between 185 nm and 195 nm the spectrum is not yet sufficiently well known, so that it is not certain how the brightness temperature goes from 4500 K 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 observed by Rottman (1974) and between 190.5 - 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.

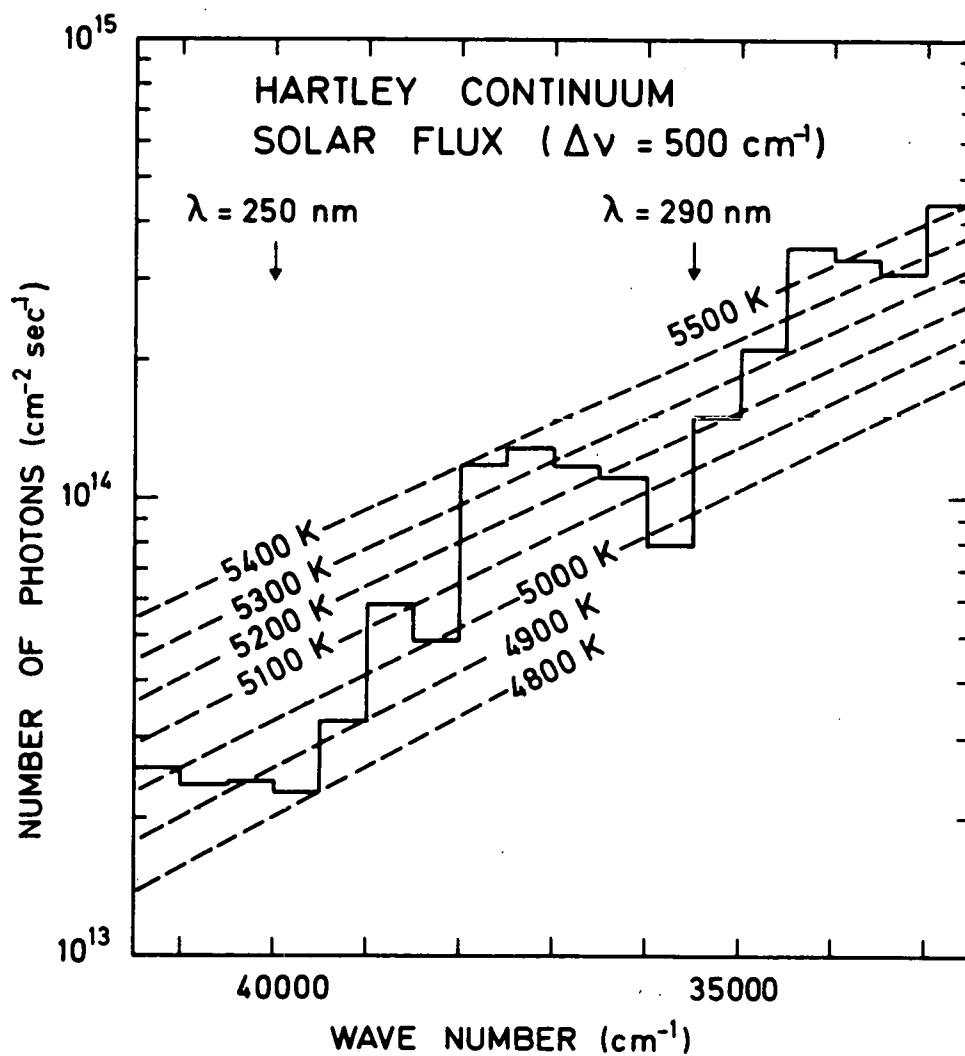


Fig. 14.- Number of photons available at the top of the terrestrial atmosphere for the mean sun to earth distance between 241 nm and 308 nm. Values in $\text{cm}^{-2} \text{ sec}^{-1}$ for $\Delta\nu = 500 \text{ cm}^{-1}$ as given in Table III.

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 (Bolland 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), new precise absolute measurements are needed between 180 nm 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 nm and 242.4 nm and are reproduced in Table II for $\Delta\nu = 500 \text{ cm}^{-1}$. Fig. 13 exhibits the observed and computed values for various brightness temperatures between 4700 K and 5200 K. The strong discontinuity near 208.7 nm is revealed by the transition from 4800 K 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 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 (± 5 percent) with Broadfoot's data. The number of photons $\text{cm}^{-2} \text{ sec}^{-1}$ for $\Delta\nu = 500 \text{ cm}^{-1}$ are given in Table III. The spectrum has been plotted in Fig. 14 with the curves for various solar brightness temperatures between 4800 K and 5500 K.

TABLE II.- Solar flux* in the spectral region of the Herzberg continuum of O₂ (Photons cm⁻² sec⁻¹ for Δν= 500 cm⁻¹ at the top of the earth's atmosphere for mean sun-earth distance).

N° (**)	Δν (cm ⁻¹)	λ (nm)	q (cm ⁻² sec ⁻¹)
58	50500 - 51000	196.1 - 198.0	1.01 x 10 ¹²
59	50000 - 50500	198.0 - 200.0	1.20
60	49500 - 50000	200.0 - 202.0	1.44
61	49000 - 49500	202.0 - 204.1	1.80
62	48500 - 49000	204.1 - 206.2	2.08
63	48000 - 48500	206.2 - 208.3	2.45
64	47500 - 48000	208.3 - 210.5	5.09
65	47000 - 47500	210.5 - 212.8	7.12
66	46500 - 47000	212.8 - 215.0	9.23
67	46000 - 46500	215.0 - 217.4	8.42
68	45500 - 46000	217.4 - 219.8	1.20 x 10 ¹³
69	45000 - 45500	219.8 - 222.2	1.22
70	44500 - 45000	222.2 - 224.7	1.77
71	44000 - 44500	224.7 - 227.3	1.60
72	43500 - 44000	227.3 - 229.9	1.96
73	43000 - 43500	229.9 - 232.6	1.97
74	42500 - 43000	232.6 - 235.3	1.70
75	42000 - 42500	235.3 - 238.1	2.00
76	41500 - 42000	238.1 - 241.0	1.77
77	41000 - 41500	241.0 - 243.9	2.58

(*) Based on Simon (1974b) from 58 to 72 and Broadfoot (1972) from 73 to 77.

(**) Nomenclature used by Ackerman (1971).

TABLE III.- Solar flux (*) in the spectral region of the Hartley bands of O_3 (Photons $cm^{-2} sec^{-1}$ for $\Delta\nu = 500 cm^{-1}$ at the top of the earth's atmosphere for mean sun-earth distance).

$N^\circ (**)$	$\Delta\nu (cm^{-1})$	$\Delta\lambda (nm)$	$q(cm^{-2} sec^{-1})$
77	41000 - 41500	241.0 - 243.9	2.58×10^{13}
78	40500 - 41000	243.9 - 246.9	2.35
79	40000 - 40500	246.9 - 250.0	2.38
80	39500 - 40000	250.0 - 253.2	2.28
81	39000 - 39500	253.2 - 256.4	3.24
82	38500 - 39000	256.4 - 259.7	5.83
83	38000 - 38500	259.7 - 263.2	4.89
84	37500 - 38000	263.2 - 266.7	1.19×10^{14}
85	37000 - 37500	266.7 - 270.3	1.29
86	36500 - 37000	270.3 - 274.0	1.17
87	36000 - 36500	274.0 - 277.8	1.11
88	35500 - 36000	277.8 - 281.7	7.85×10^{13}
89	35000 - 35500	281.7 - 285.7	1.50×10^{14}
90	34500 - 35000	285.7 - 289.9	2.12
91	34000 - 34500	289.9 - 294.1	3.56
92	33500 - 34000	294.1 - 298.5	3.33
93	33000 - 33500	298.5 - 303.0	3.08
94	32500 - 33000	303.0 - 307.7	4.39

(*) Based on Simon (1974b) from 90 to 94 and Broadfoot (1972) from 77 to 93.

(**) Nomenclature used by Ackerman (1971).

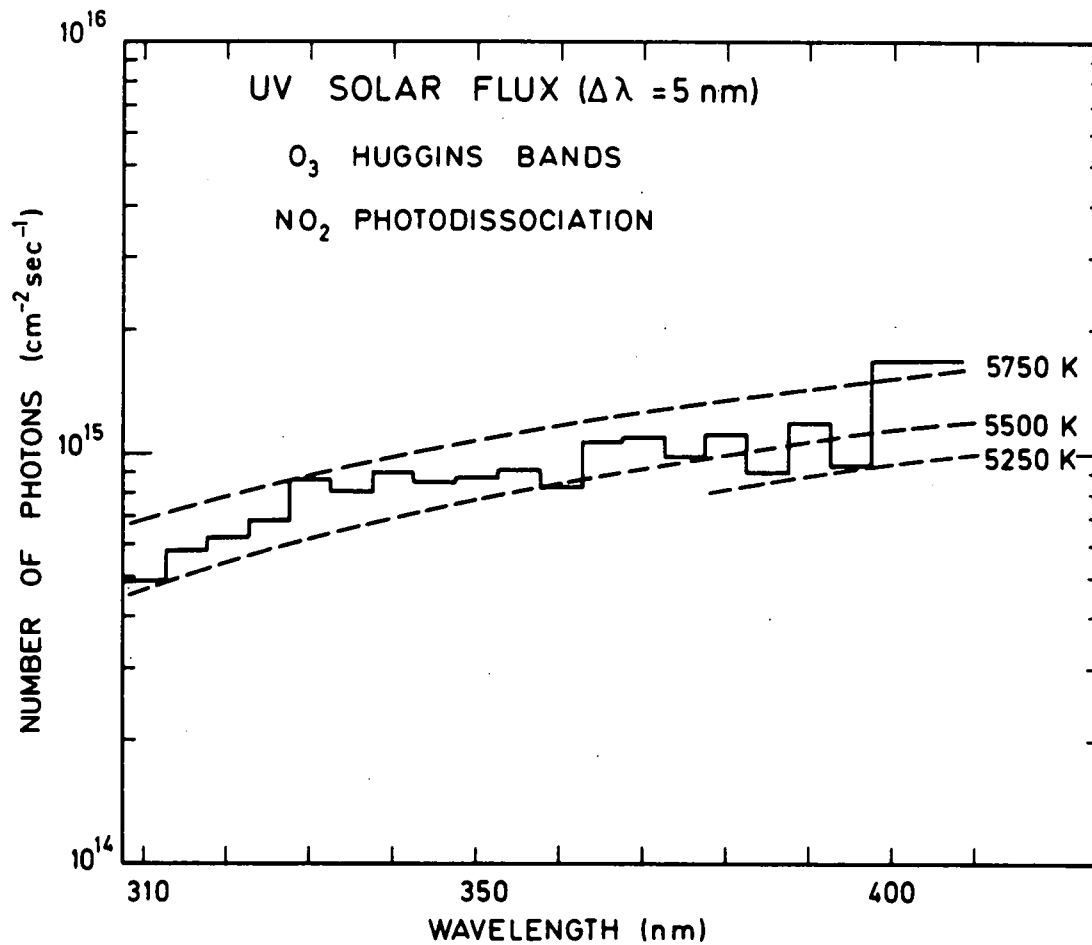


Fig. 15.- Number of photons available at the top of the terrestrial atmosphere for the mean sun to earth distance between 310 nm and 400 nm. Values in $\text{cm}^{-2} \text{sec}^{-1}$ for $\Delta\lambda = 5 \text{ nm}$ as given in Table IV.

In the spectral region ($\lambda > 310$ nm) of the solar ultraviolet flux transmitted to the ground, many observations have been made. 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 (1974b) 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 nm and 400 nm with an error which may reach 10 percent in certain intervals. Adopted values are provided in Table IV. 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: $1.99 \text{ cal cm}^{-2} \text{ min}^{-1}$ instead of $1.95 \text{ cal cm}^{-2} \text{ min}^{-1}$. The values used for $\Delta \lambda = 5$ nm are about 10% lower than data tabulated by Ackerman (1971) ; they are shown in Fig. 15 and correspond to solar fluxes equivalent to brightness temperatures between 5500 K 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 - 400 nm spectral region, and the numerical results, which can be used for the calculation of photodissociation coefficients, are given in Table V 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 IV.- Solar flux (*) in the spectral region of the Huggins bands of O_3 and photodissociation continuum of NO_2 (Photons $cm^{-2} sec^{-1}$ for $\Delta \lambda = 5 \text{ nm}$ (50 Å) at the top of the earth's atmosphere for mean sun-earth distance)

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

(*) Derived from Arvesen et al. (1969) and reduced to a solar constant value of $1.95 \text{ cal cm}^{-2} \text{ min}^{-1}$. See text.

(**) Nomenclature used by Ackerman (1971).

TABLE V.- Solar flux (*) in the visible part of the spectrum ($q = 10^{-15}$ photons $\text{cm}^{-2} \text{sec}^{-1}$ for $\Delta\lambda = 5 \text{ nm}$ at the top of the terrestrial atmosphere for mean sun-earth distance ; $\lambda \pm 2.5 \text{ nm}$).

N°(**)	λ (nm)	q	N°	λ (nm)	q	N°	λ (nm)	q
113	400	1.69	140	535	2.51	167	670	2.61
114	405	1.70	141	540	2.49	168	675	2.62
115	410	1.84	142	545	2.55	169	680	2.62
116	415	1.97	143	550	2.53	170	685	2.57
117	420	1.95	144	555	2.54	171	690	2.52
118	425	1.81	145	560	2.50	172	695	2.60
119	430	1.67	146	565	2.57	173	700	2.58
120	435	1.98	147	570	2.58	174	705	2.52
121	440	2.02	148	575	2.67	175	710	2.51
122	445	2.18	149	580	2.67	176	715	2.48
123	450	2.36	150	585	2.70	177	720	2.45
124	455	2.31	151	590	2.62	178	725	2.48
125	460	2.39	152	595	2.69	179	730	2.45
126	465	2.38	153	600	2.63	180	735	2.44
127	470	2.39	154	605	2.68	181	740	2.39
128	475	2.44	155	610	2.66	182	745	2.40
129	480	2.51	156	615	2.59	183	750	2.41
130	485	2.30	157	620	2.69	184	755	2.40
131	490	2.39	158	625	2.61	185	760	2.38
132	495	2.48	159	630	2.62	186	765	2.34
133	500	2.40	160	635	2.62	187	770	2.32
134	505	2.46	161	640	2.63	188	775	2.30
135	510	2.49	162	645	2.60	189	780	2.33
136	515	2.32	163	650	2.55	190	785	2.34
137	520	2.39	164(***)	655	2.48	191	790	2.29
138	525	2.42	165	660	2.57	192	795	2.29
139	530	2.55	166	665	2.61	193	800	2.27

(*) Derived from Table VII of Arvesen et al. (1969) and reduced to a solar constant value of $1.95 \text{ cal cm}^{-2} \text{ min}^{-1}$.

(**) Nomenclature used by Ackerman (1971)

(***) Extension of nomenclature.

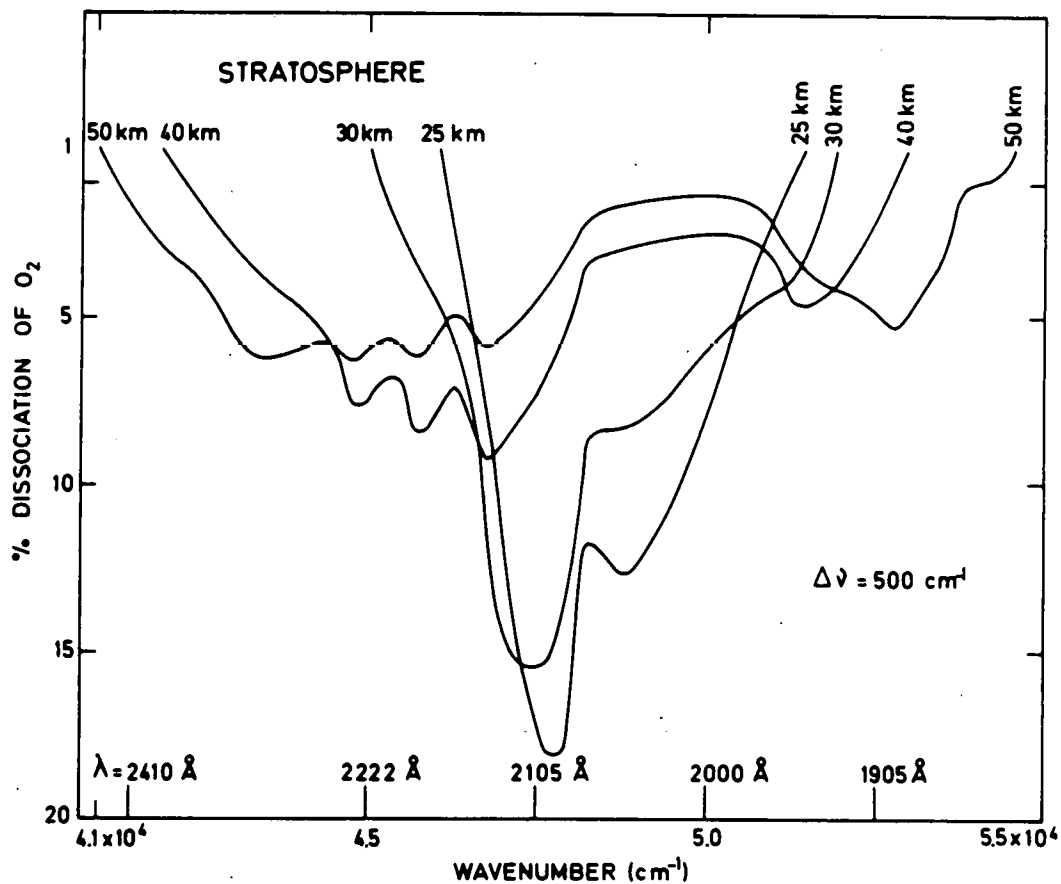


Fig. 16.- Dissociation of molecular oxygen in the stratosphere according to the wavelength for various heights from the stratopause to 25 km for overhead sun conditions. The percentages are given for spectral range $\Delta\nu = 500 \text{ cm}^{-1}$. Standard conditions.

9. 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 account of 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 VI 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 VII 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 VIII are used, it can be shown with the solar fluxes of Table II 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 stratosphere as illustrated in Fig. 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. With the penetration of solar radiation in the stratosphere the important part of the spectrum corresponds to the region

TABLE VI.- Standard Atmosphere, latitude 45°

Altitude (km)	Temperature (K)	Scale height (km)	Pressure (mb)	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	256	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}

TABLE VII.- Standard atmosphere, latitude 45° constituents [concentrations
(n) and totals (N)]

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}

TABLE VIII.- Absorption coefficients of O_2 and O_3 for $\Delta\nu = 500 \text{ cm}^{-1}$
 (Ackerman, 1971) in the Herzberg continuum .

No	$\Delta \nu$	$\sigma(O_2), (\text{cm}^2)$	$\sigma(O_3), (\text{cm}^2)$
77	41000 - 41500	6.74×10^{-25}	9.00×10^{-18}
76	41500 - 42000	1.75×10^{-24}	7.97
75	42000 - 42500	2.44	6.86
74	42500 - 43000	3.09	5.79
73	43000 - 43500	3.76	4.83
72	43500 - 44000	4.40	4.00
71	44000 - 44500	5.03	3.24
70	44500 - 45000	5.65	2.55
69	45000 - 45500	6.28	1.97
68	45500 - 46000	6.92	1.52
67	46000 - 46500	7.60	1.17
66	46500 - 47000	8.28	8.57×10^{-19}
65	47000 - 47500	8.93	6.26
64	47500 - 48000	9.55	4.84
63	48000 - 48500	1.00×10^{-23}	4.11
62	48500 - 49000	1.05	3.51
61	49000 - 49500	1.14	3.26
60	49500 - 50000	(1.5×10^{-23})	3.26
59	50000 - 50500	(2.0×10^{-23})	3.30
58	50500 - 51000	(3.0×10^{-23})	3.69×10^{-19}

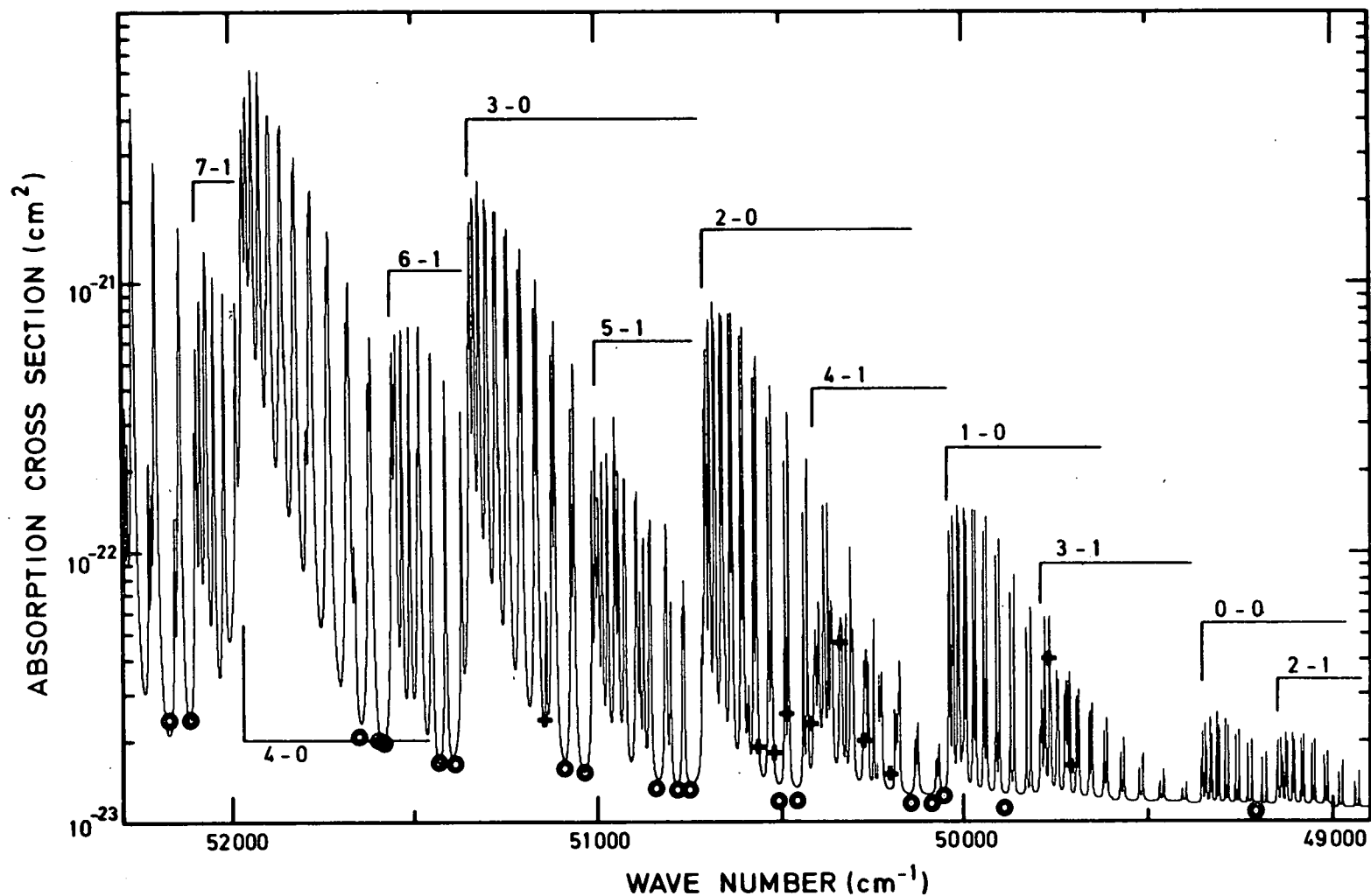


Fig. 17.- Rotational structure of the Schumann-Runge bands of O_2 at 300 K (Ackerman et al., 1970) from (0-0) to (7-1). Theoretical determination with laboratory data are indicated by crosses and with experimental continuum by Ogawa (1971) by circles. Effect of the Herzberg continuum is important for $\nu < 51000 \text{ cm}^{-1}$.

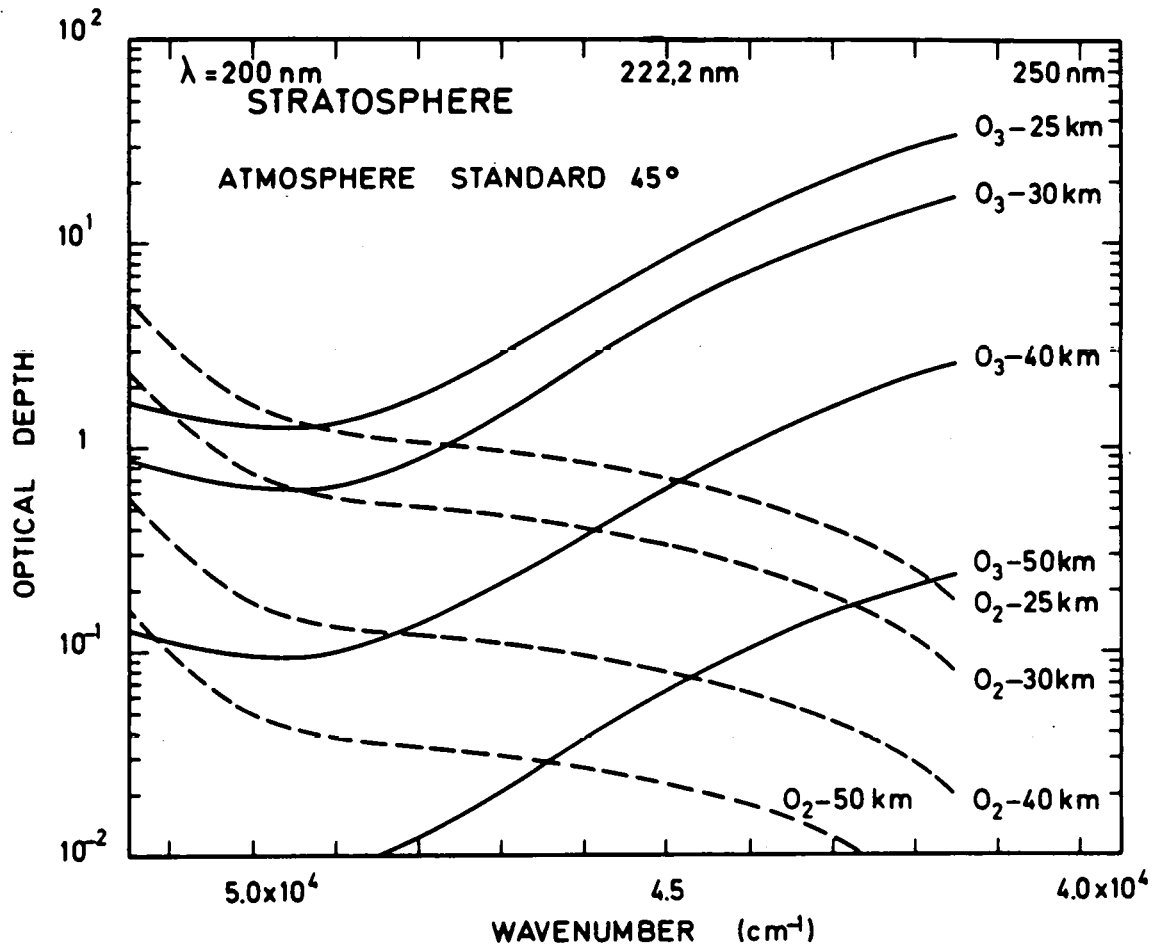


Fig. 18.- Optical depth of molecular oxygen and ozone absorption in the stratosphere in the spectral region leading to O₂ dissociation at various heights.

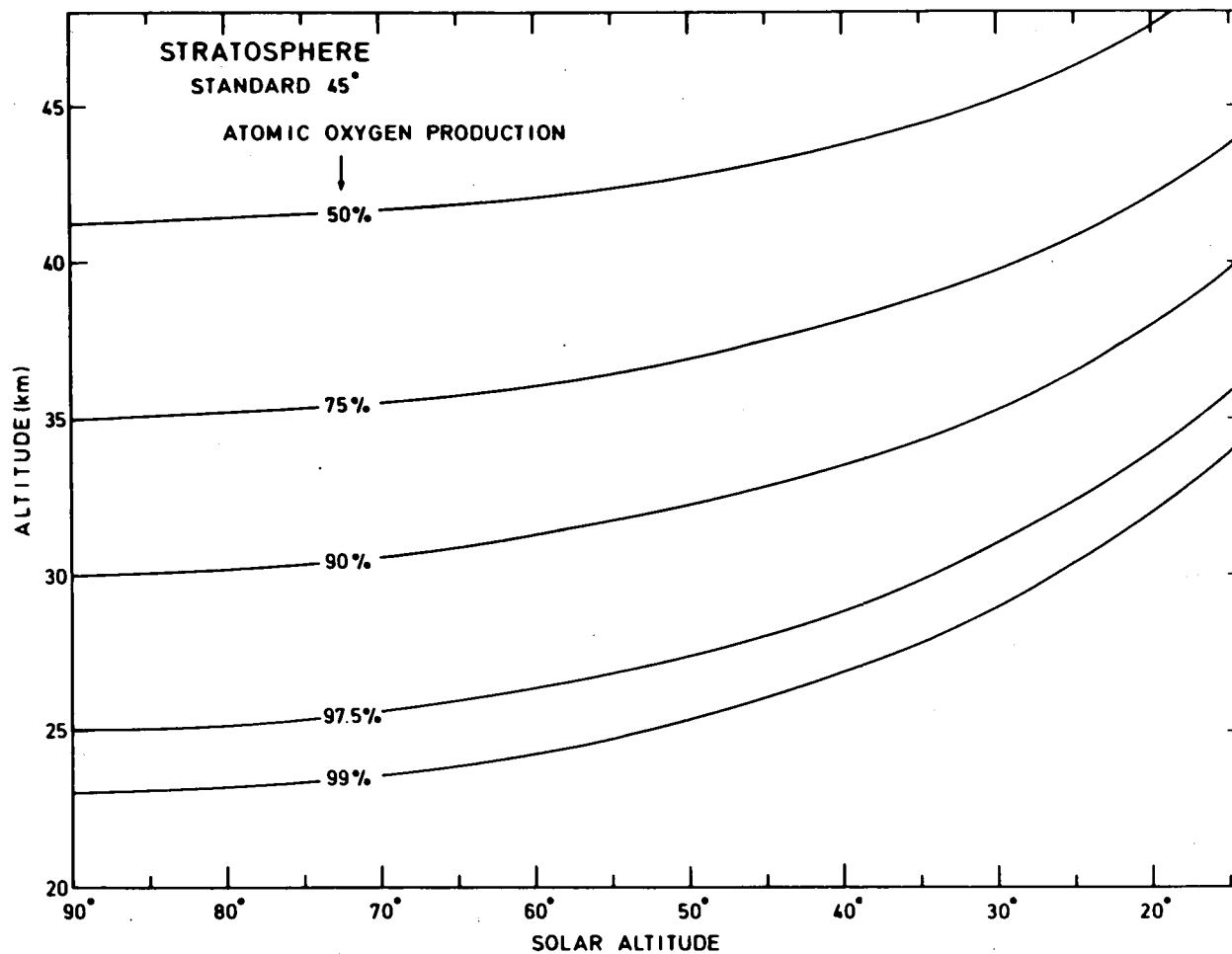


Fig. 19.- Total atomic oxygen production (%) for various altitudes of the sun ; an overhead sun ($h_{\odot} = 90^{\circ}$) to $h_{\odot} = 20^{\circ}$.

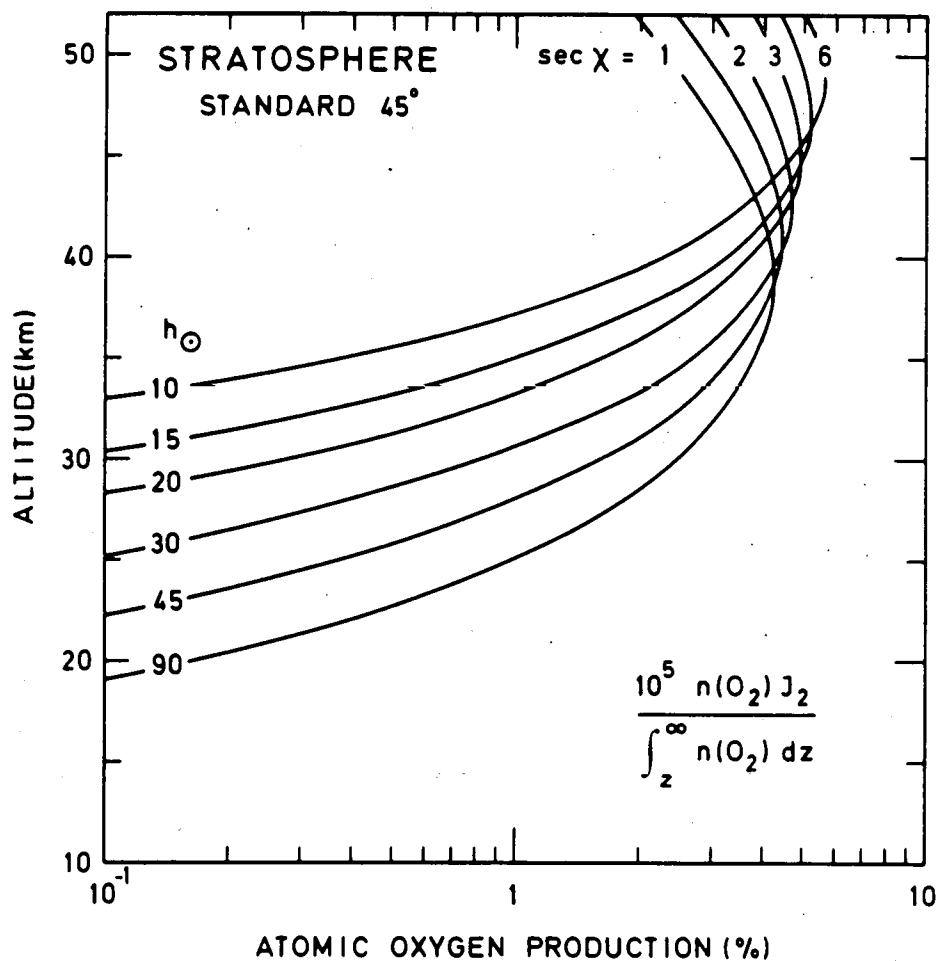


Fig. 20.- Vertical distribution of the atomic oxygen production (%) for various altitudes of the sun ; $h_{\odot} = 90^{\circ}$, overhead sun. A layer of 1 km thickness is considered.

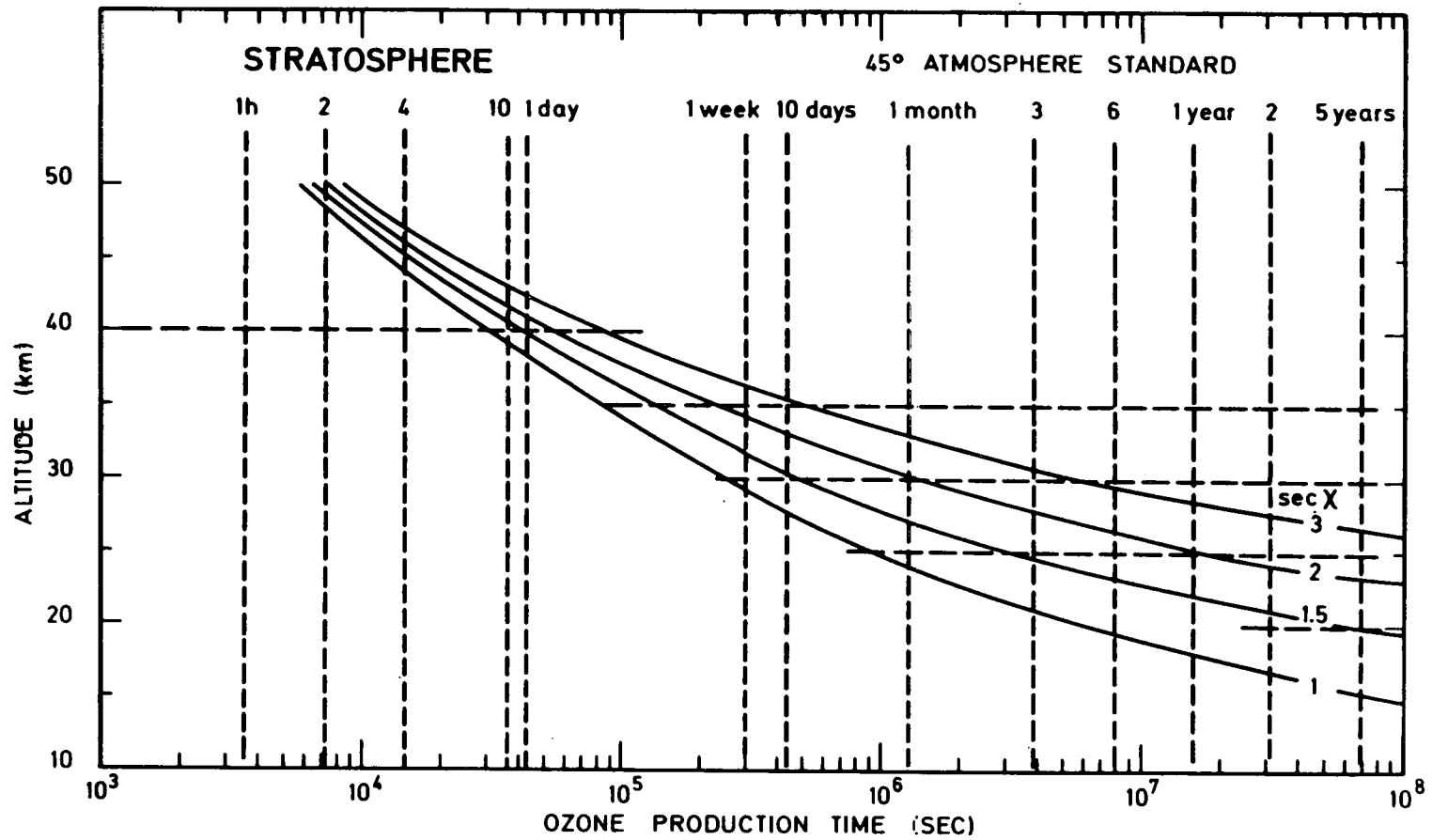


Fig. 21.- Production times of stratospheric ozone (concentrations given in Table VII) for various solar zenith angles.

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 a 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 Fig. 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 Fig. 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 Fig. 19 where various percentages are shown versus the solar zenith angle. More than 50 percent are 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. Fig. 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.

It is also possible to derive under these standard conditions the time necessary to produce the ozone concentration as given in Table VI. The variation with altitude changes as depicted in Fig. 21. Above 40 km, it

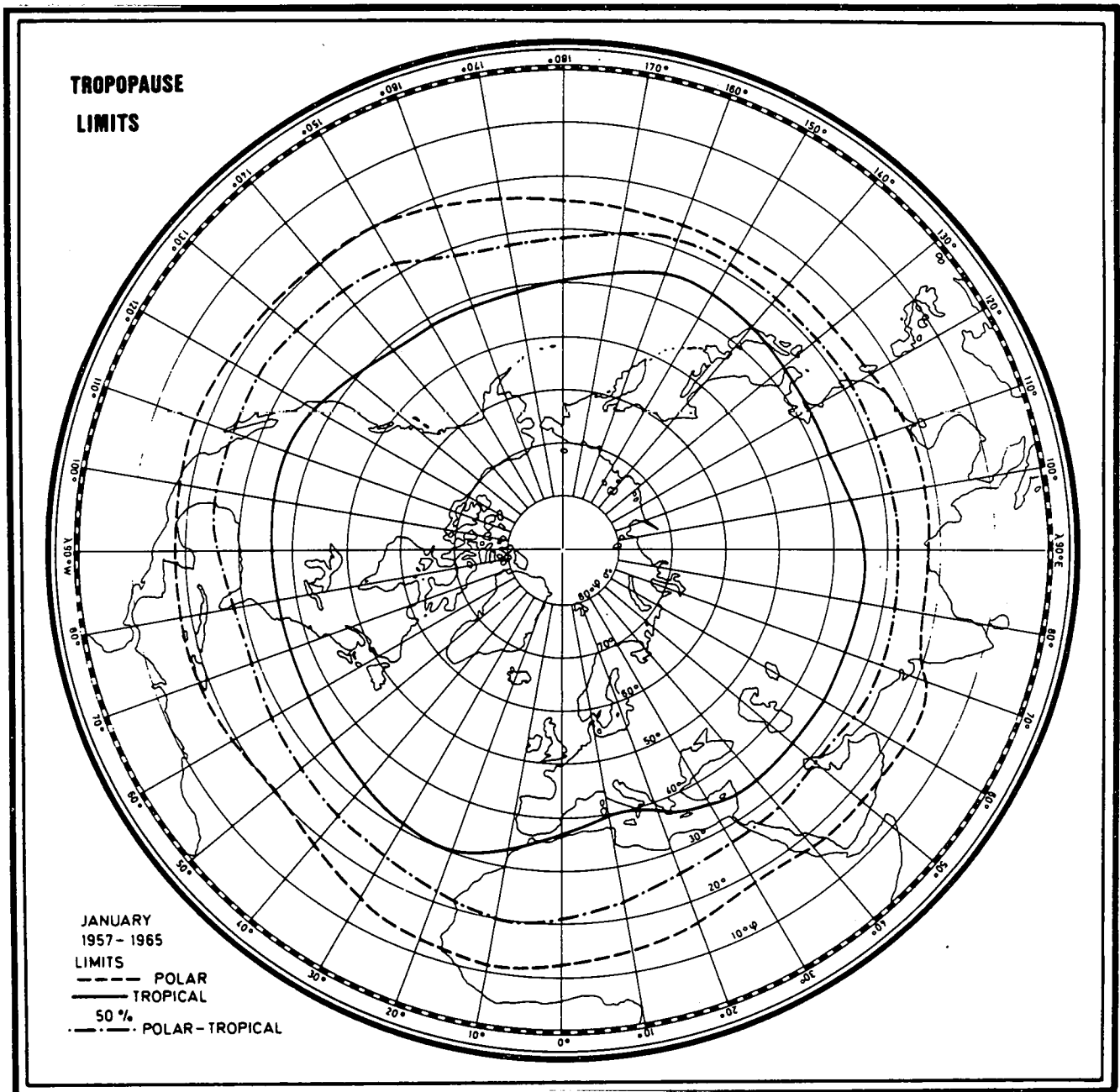


Fig. 22.- Limits of the lower stratospheric regions indicated by the geographic distribution of the polar and tropical tropopause in January (1957 to 1965) in the northern hemisphere, Makhover (1972).

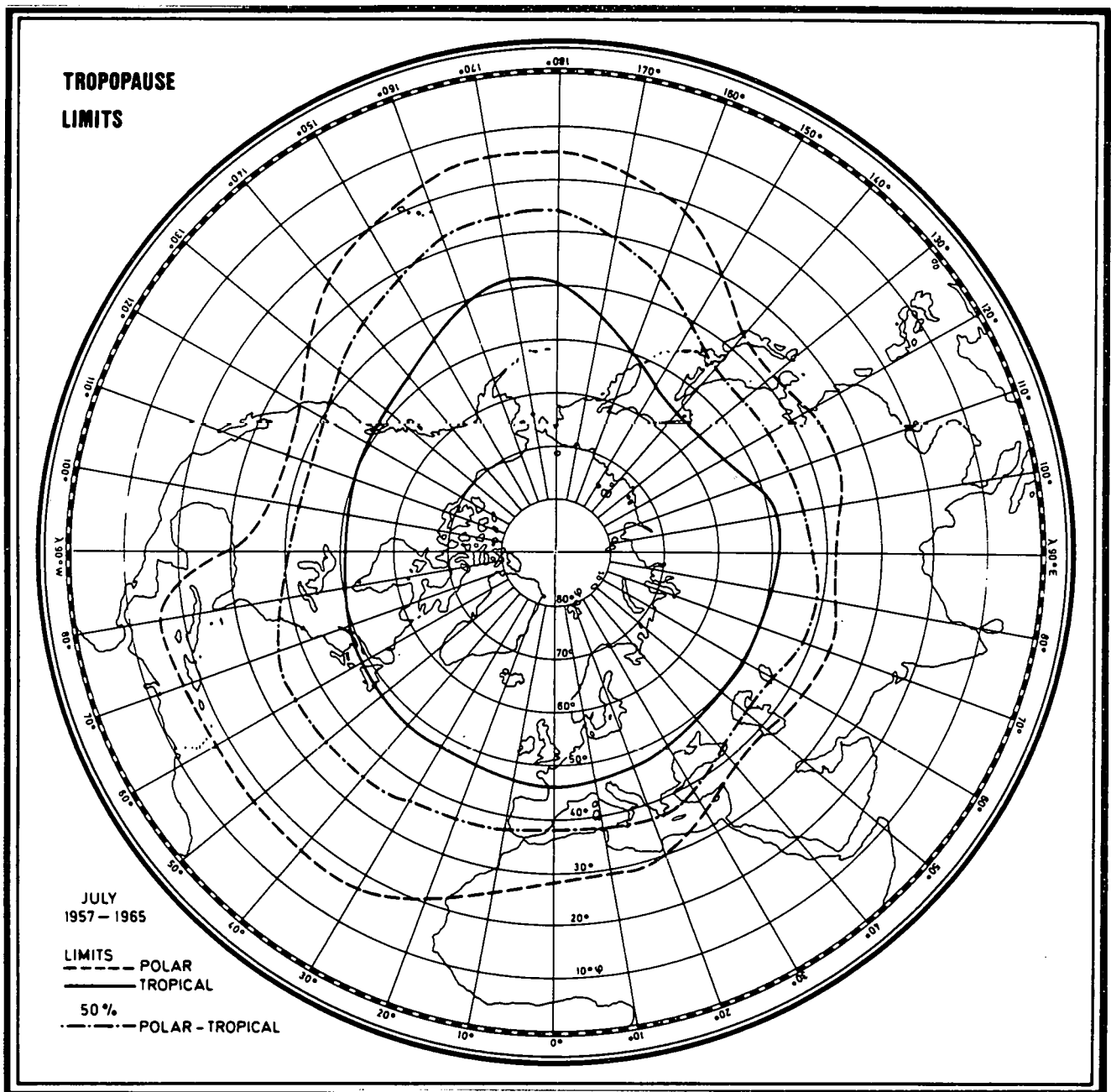


Fig. 23.- Limits of the lower stratospheric regions indicated by the geographic distribution of the polar and tropical tropopause in July (1957 to 1965) in the northern hemisphere ; Makhover (1972).

always requires less than a day; at 25 km, the times are not less than one 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 two years would be necessary to produce the observed ozone and transport is therefore responsible.

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 V. 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 action 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 (1962) from 11 km 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 must be considered, their variation must be taken into account when lower boundary conditions are introduced into the calculation of stratospheric models. Fig. 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 (Fig. 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 (Fig. 23), there is an extension of the stratospheric regions with tropical tropopause towards 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 Fig. 22 and 23 that there is a considerable

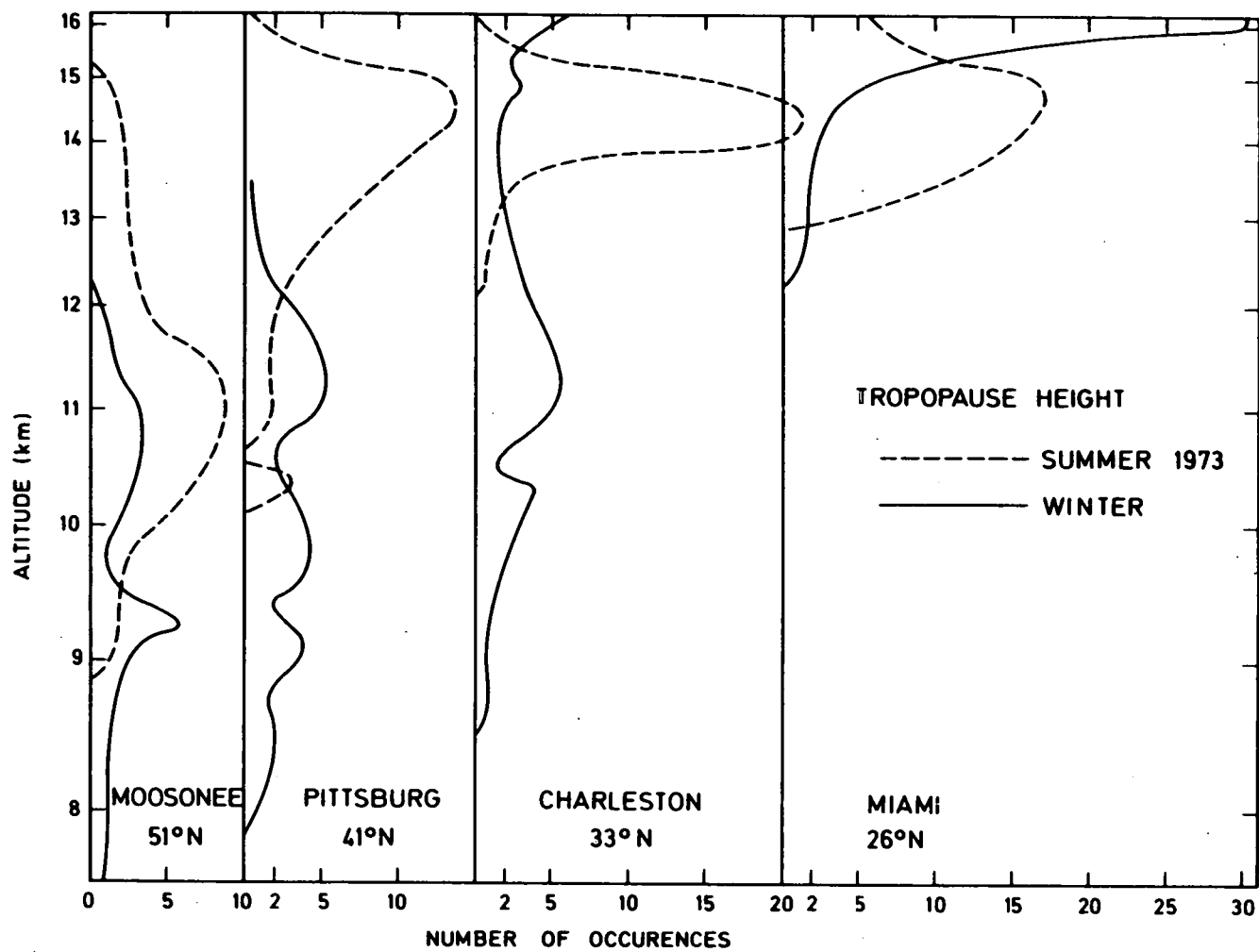


Fig. 24.- Variations of tropopause heights for summer and winter conditions at 4 stations between 21 and 51° N. Downie (1974).

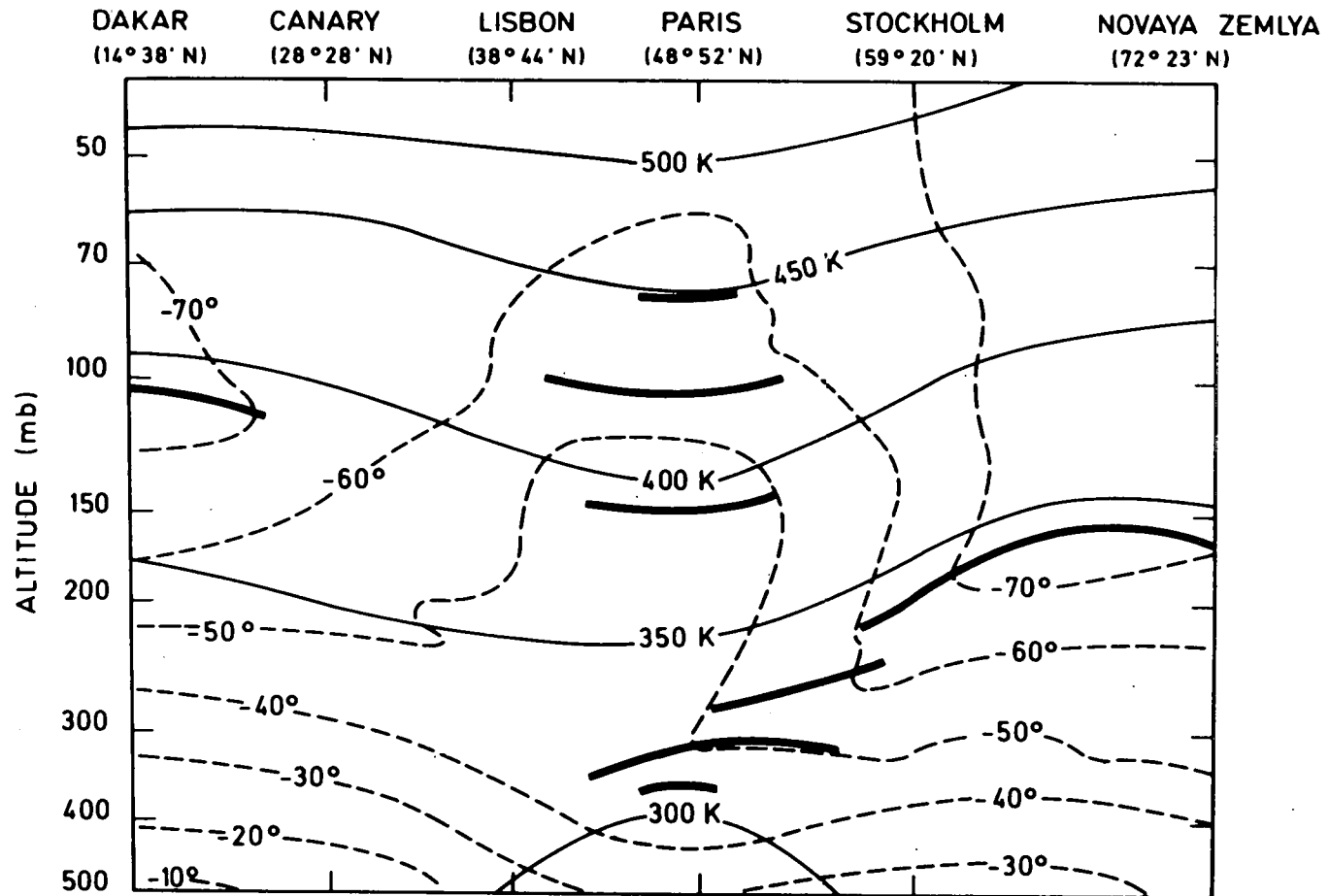


Fig. 25.- Vertical profiles from tropical regions to polar regions, February 17, 1967, OOGMT, from Piaget (1971). Isentropic lines in K, and isothermal lines in C. The various conventional tropopauses are indicated by heavy lines. Details in Piaget (1971).

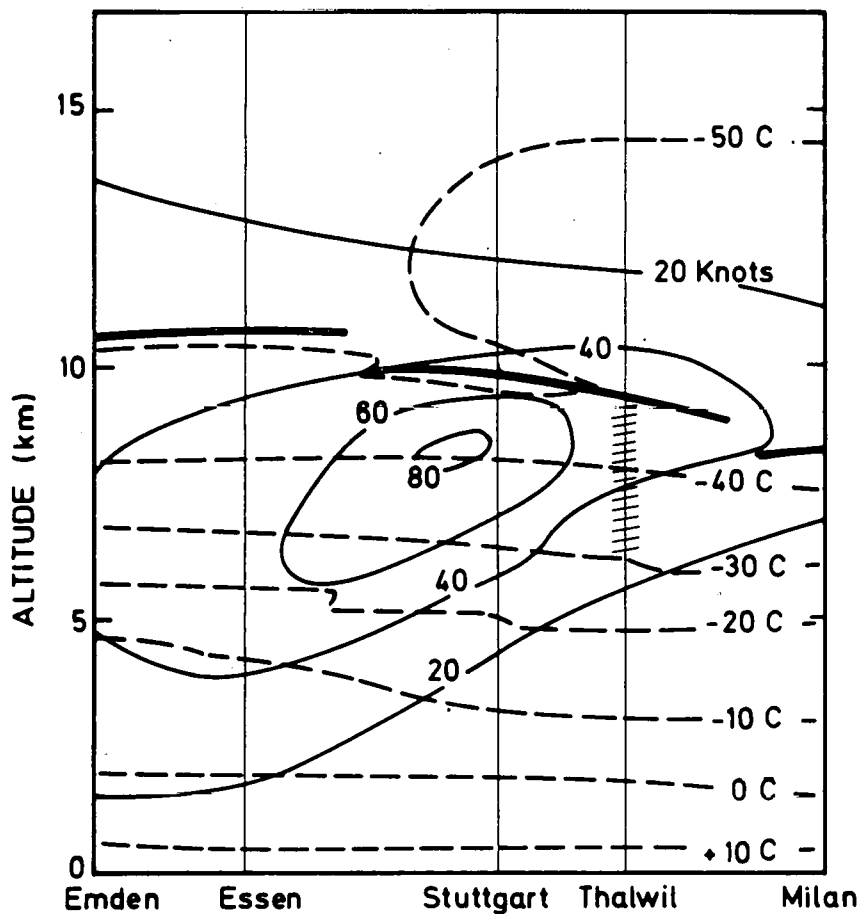


Fig. 26.- Vertical profile from Emden ($53^{\circ}4N$; $07^{\circ}2E$) to Thawill ($47^{\circ}3N$; $08^{\circ}5E$) and Milan ($45^{\circ}4N$; $09^{\circ}3E$), June 12, 1967 at 12 GMT ; from Piaget (1969, 1971). Isothermal lines in $^{\circ}C$; isoplethic lines of the wind speed in knots ; heavy lines at the tropopause levels. Regions of ozone increase at Thawill is indicated by a shading.

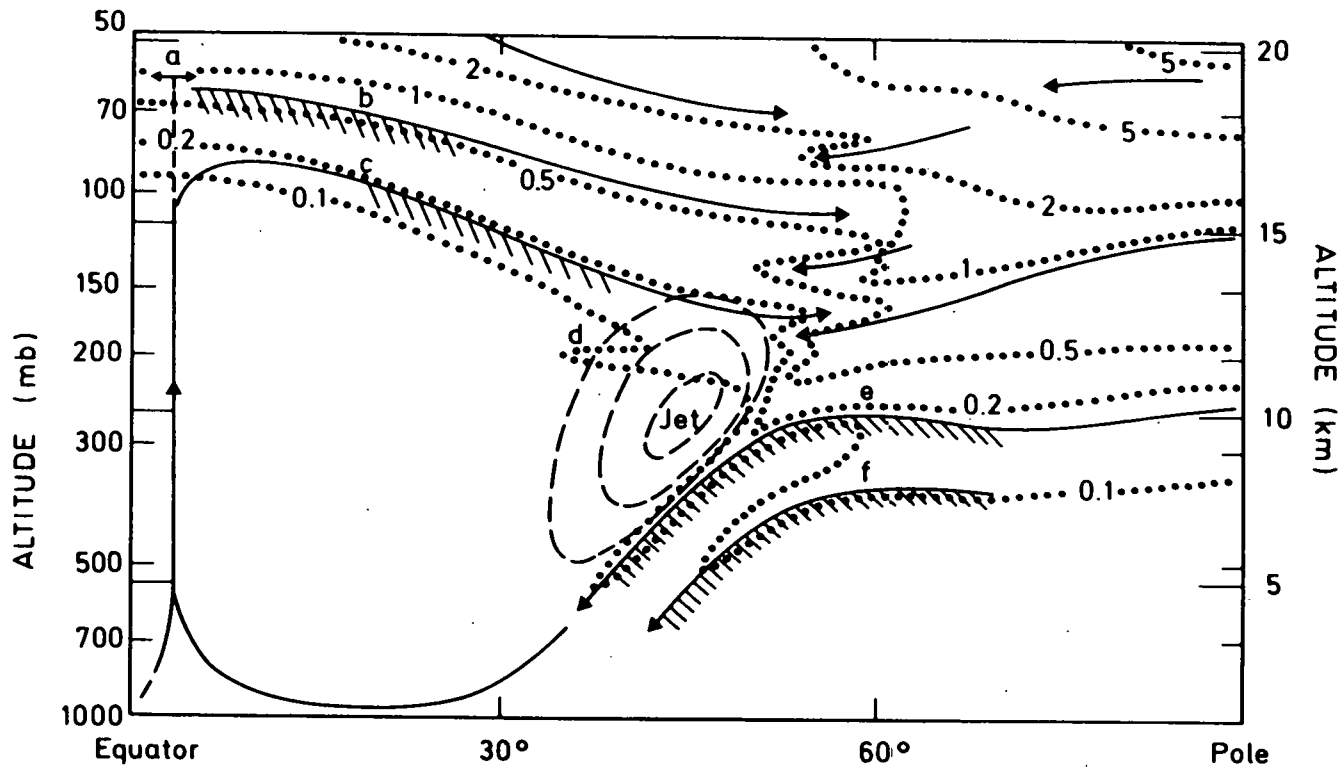


Fig. 27.- Schematic meridional profile of exchanges between the stratosphere and troposphere, according to Piaget (1971). Isentropic trajectories are represented by continuous lines ; ozone mixing ratios ($\mu\text{g/g}$) by dotted lines ; isopleths of wind speed by dashed lines and conventional tropopauses by shading. The curves a, b, c, d, e and f are described in the text.

variability which must be considered. An example deduced from a recent analysis by Downie (1974) is illustrated by the various curves (Fig. 24) which give, at various latitudes, the number of occurrences 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 (1969, 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 Fig. 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 in a steady state and with constant lower boundary condition. Another indication is given by the vertical cross section illustrated by Fig. 26 where a specific ozone increase is indicated by three conventional tropopauses in a latitude 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 Fig. 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 (a) of the tropical stratospheric air (b) and of the tropical tropospheric air (c) which travel toward the jet stream latitudes above the conventional tropopause. The region, which is indicated (d) in Fig. 27, corresponds to the subtropical jet stream. As far as the intrusions of polar stratospheric air into the troposphere are concerned, they are illustrated by (e) which corresponds to a normal flow and by (f) which shows an additional effect associated with the

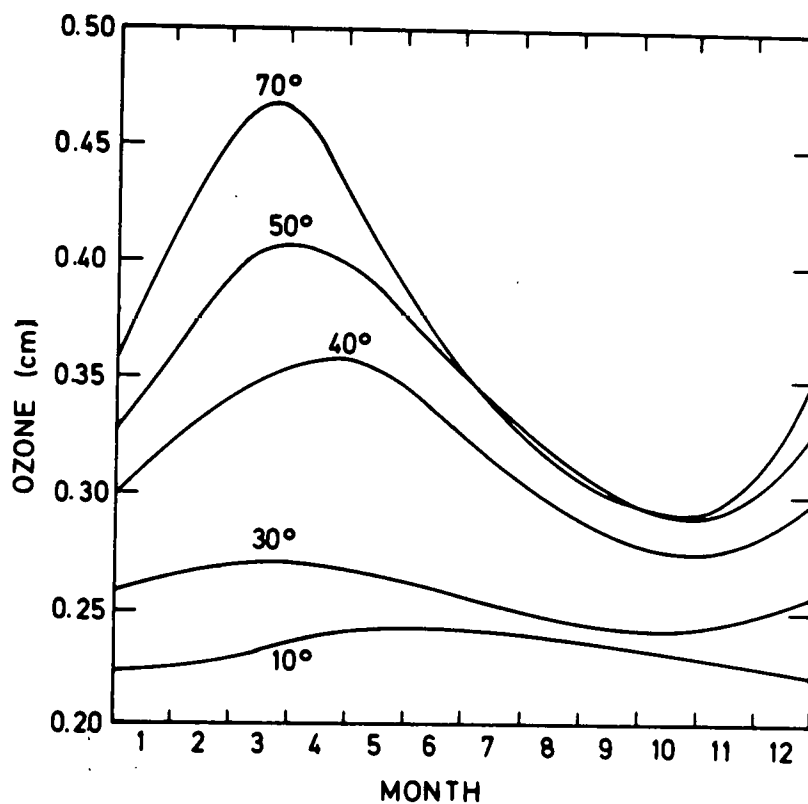


Fig. 28.- Smoothed annual variation of the total amount of ozone at 10°, 30°, 40°, 50° and 60° of N latitude, according to Dobson (1963). Ozone amount in cm (STP).

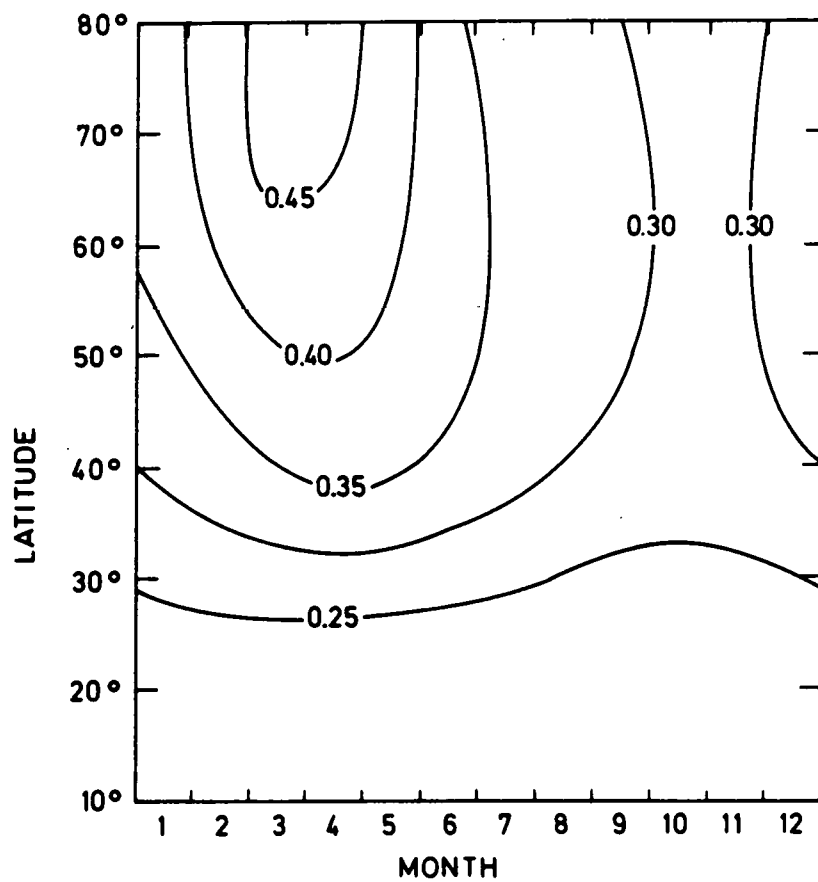


Fig. 29.- Annual distributions of the total amount of ozone (cm STP) versus latitude, according to Dobson (1963).

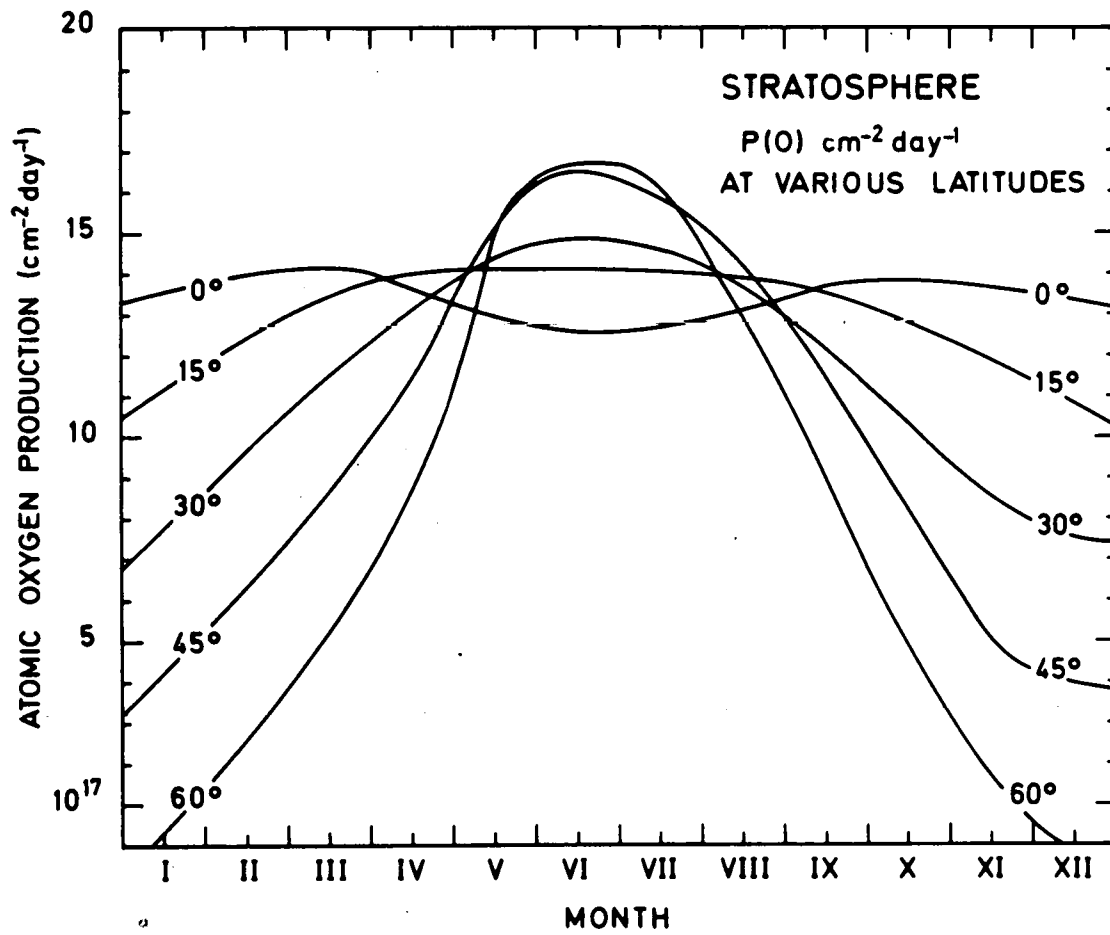


Fig. 30.- Annual distribution of atomic oxygen production ($\text{cm}^{-2} \text{ day}^{-1}$) at 0° , 15° , 30° , 45° and 60°N .

penetration of polar air inside of the cold air. Finally, it should be noticed 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 Fig. 28. The continuous curves represent conditions for which all abnormalities 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 Fig. 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 (Fig. 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 Fig. 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 $\text{cm}^{-2} \text{day}^{-1}$, is practically constant during the year. At 45° , there is a strong variation from about 3×10^{17} molecules $\text{cm}^{-2} \text{day}^{-1}$ in January to 1.6×10^{18} molecules $\text{cm}^{-2} \text{day}^{-1}$ in June-July. At latitudes greater than 60° , the winter production is negligible. There is therefore no direct association 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 three 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.

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

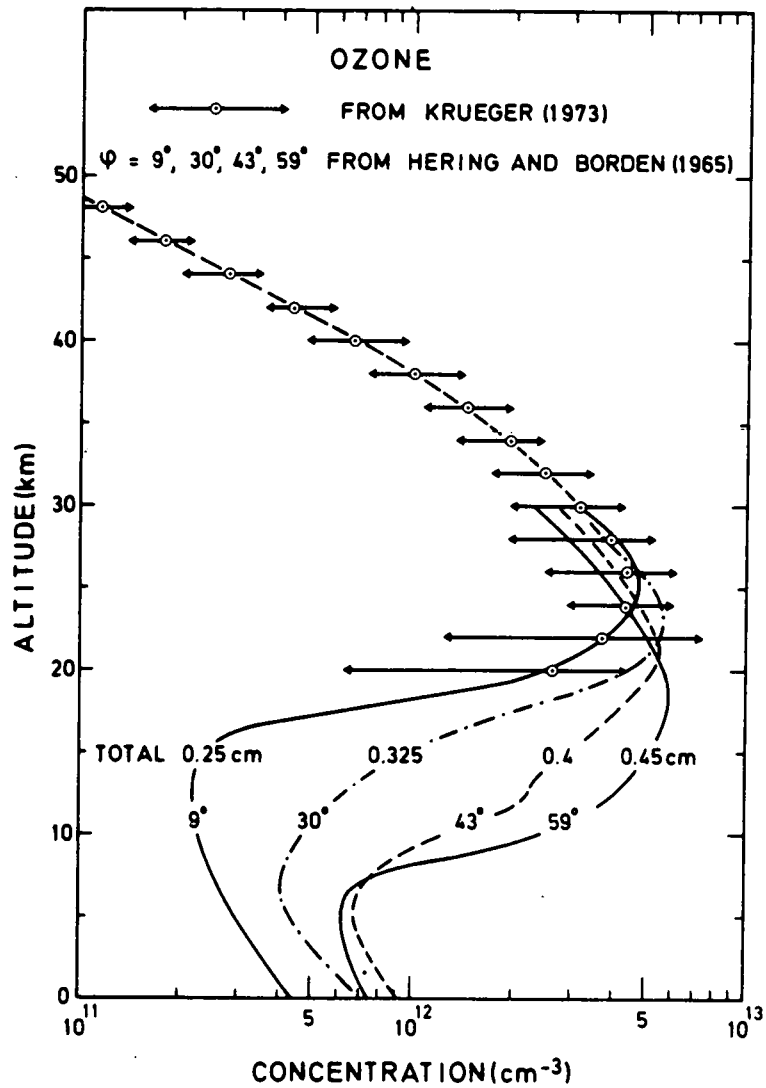


Fig. 31.- Examples of vertical distribution of ozone concentrations associated with an increase of the total amount related to latitude in the lower stratosphere.

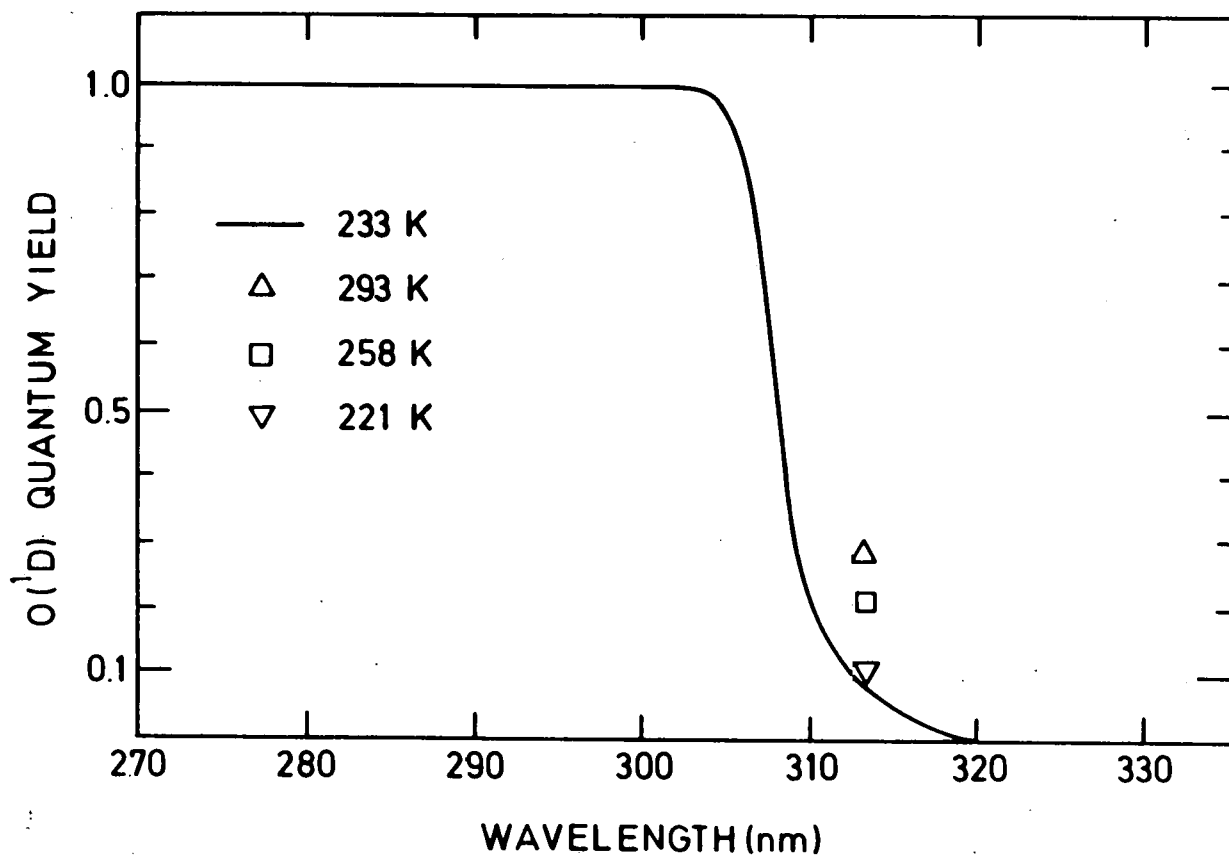


Fig. 32.- Quantum yield of $O(^1D)$ production versus wavelength. Curve at 233 K by Lin and DeMore (1973) and at $\lambda = 313$ nm at 293, 258 and 251 by Kuis et al. (1974).

concentrations below its peak. An illustration of the latitudinal variation is given in Fig. 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.

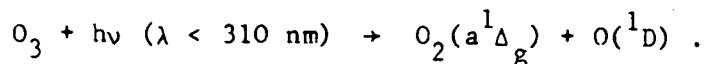
10. PHOTODISSOCIATION IN THE TROPOSPHERE AND STRATOSPHERE AND ITS EFFECTS

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 , HU_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

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

even at ground level.

In the ultraviolet, the important process is the photodissociation



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 (Fig. 32) shows that the quantum yield ϕ to be used in the lower stratosphere may be taken as follows :

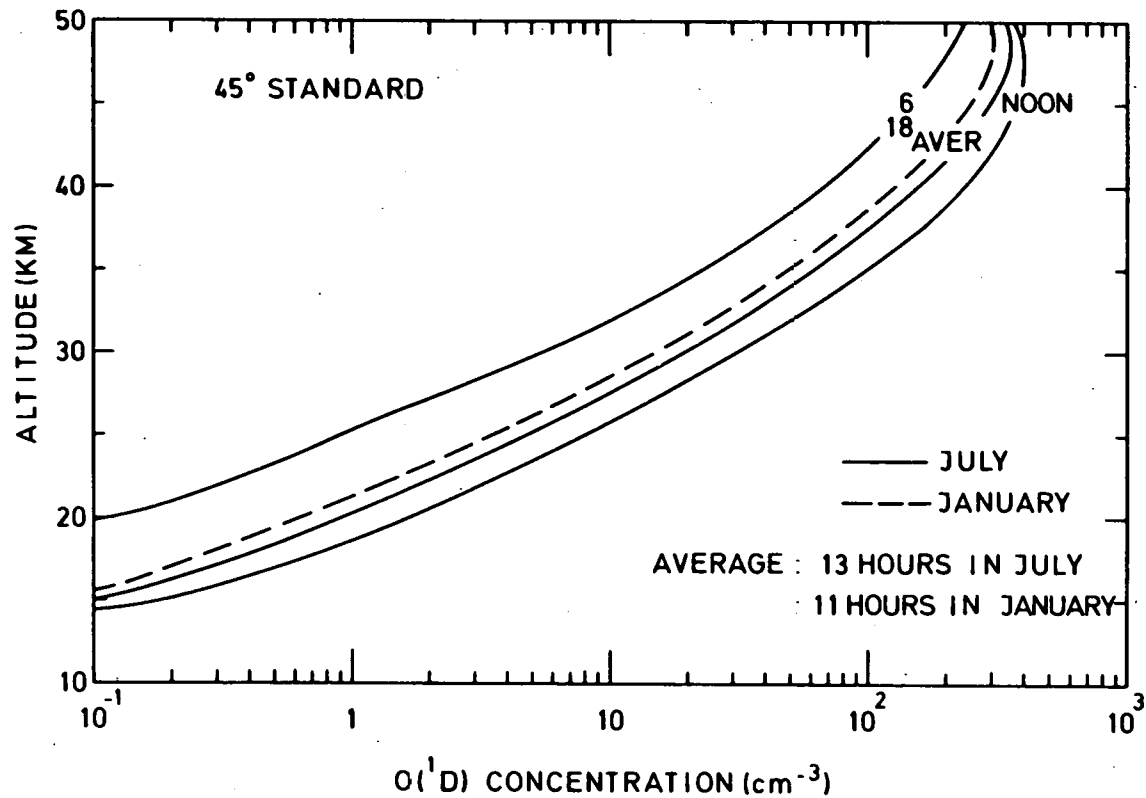


Fig. 33.- Concentration of O(¹D) atoms produced in the ozone photolysis for standard conditions as given in Table VII.

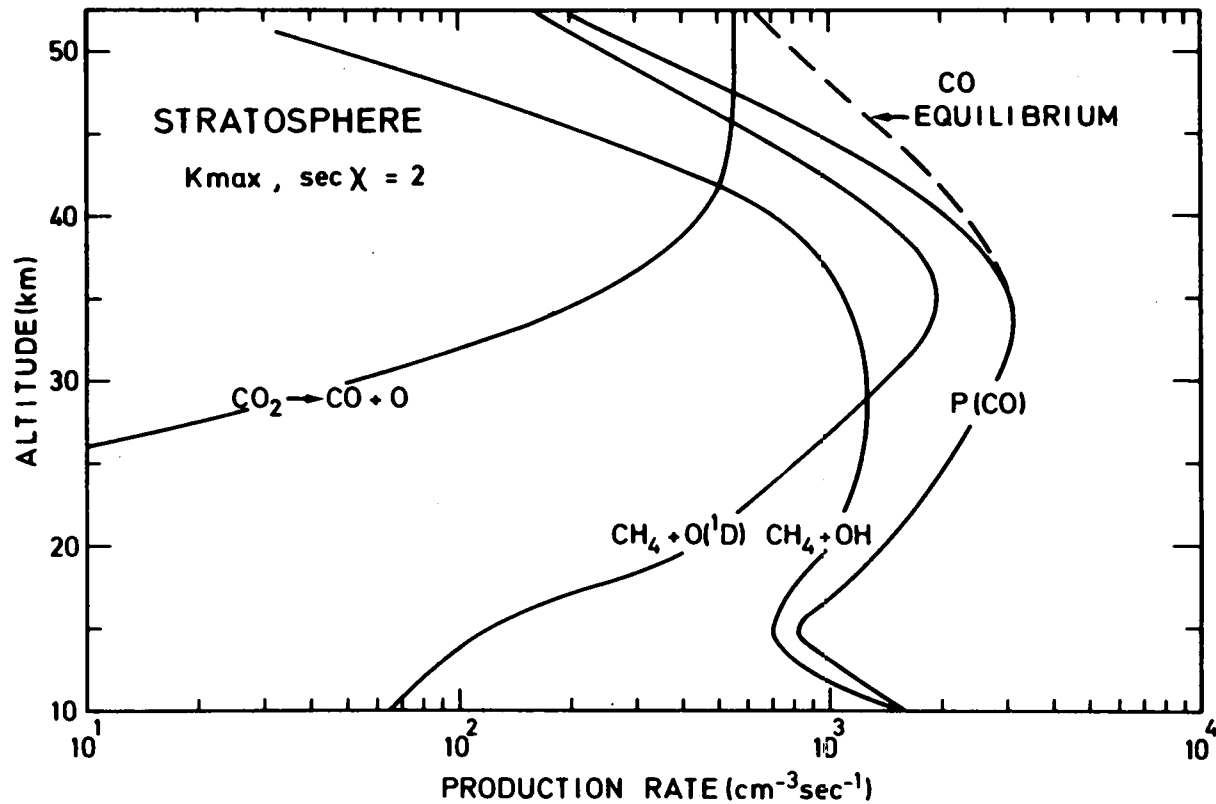


Fig. 34.- Example of reactions destroying methane and producing carbon monoxide in the stratosphere. Solar zenith angle χ with $\sec \chi = 2$ and arbitrary eddy diffusion coefficient K_{\max} are used; (Nicolet and Peetermans, 1973).

nm	300 \pm 2.5	305 \pm 2.5	310 \pm 2.5	315 \pm 2.5
$\phi(O^1D)$	1.0	0.9	0.3	0.05

The production of $O(^1D)$ atoms, which react with H_2O , 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 vertical distribution of the $O(^1D)$ concentration is given in Fig. 33 for July and January at $45^\circ N$. There is an increase from less than one $O(^1D)$ 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 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 Fig. 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. Fig. 34 also illustrates the 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 other several reactions playing significant roles.

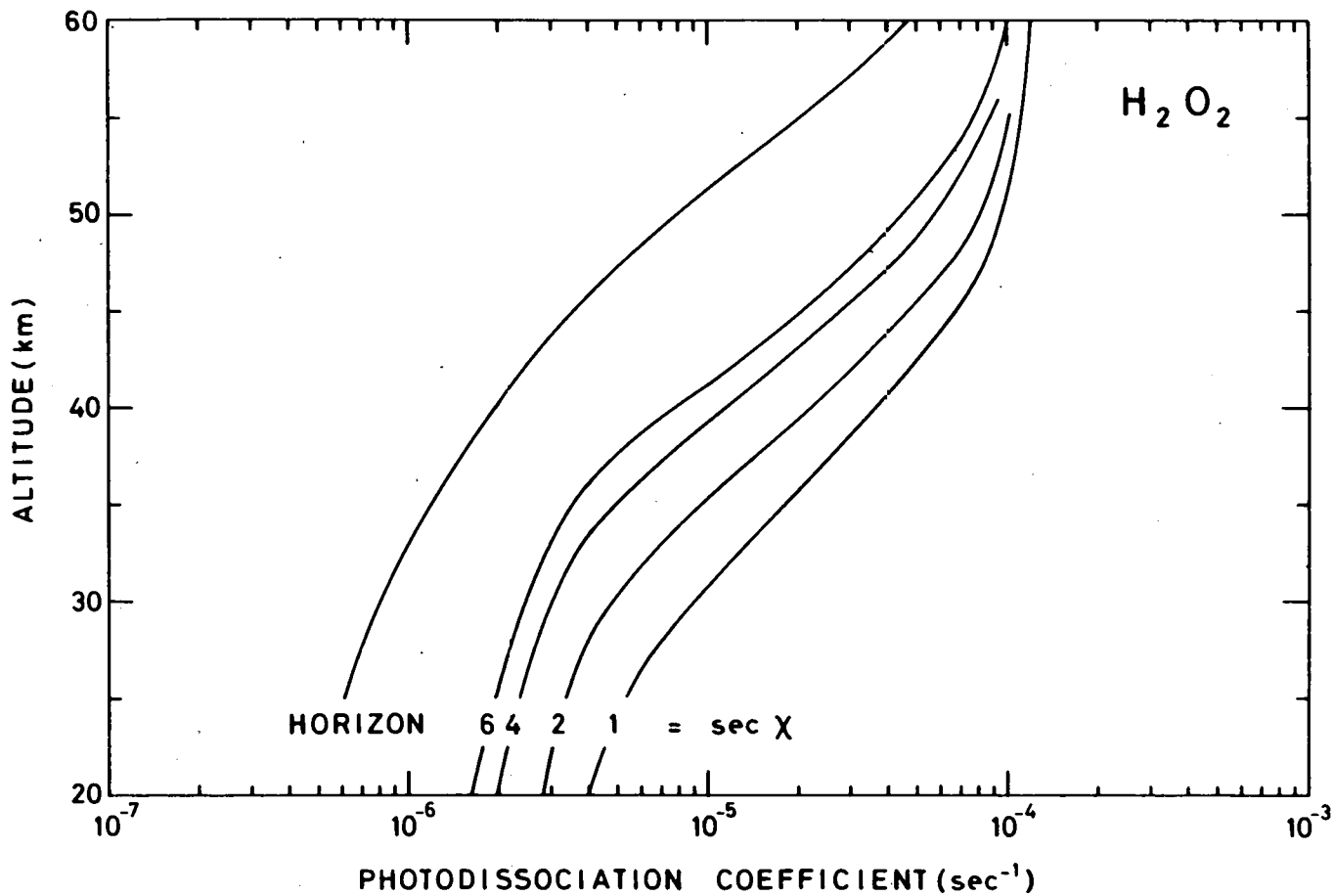


Fig. 35.- Examples of calculated vertical distributions of H₂O₂ photodissociation coefficients. Various solar zenith angles $\chi = 0$, overhead sun conditions, to $\chi = 90^\circ$, horizon (Nicolet, 1971).

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} sec^{-1} (Fig. 35) and reaches low values between 10^{-5} and 10^{-6} sec^{-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 $\lambda > 300 \text{ nm}$ which leads to a high photodissociation coefficient, the indication being that such molecules are always in photochemical equilibrium. Precise values are required for J_{NO_2} since it determines the daytime ratio $n(\text{NO}_2)/n(\text{NO})$. Various laboratory measurements of the absorption cross-sections have been made at room temperature and seem to lead to $J_{\text{NO}_2} = 6 \pm 2 \times 10^{-2} \text{ sec}^{-1}$ at ground level (Stedman et al., 1975a). However, scattering effects (Callis, 1974) must be introduced in 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 the variation of solar zenith angles.

The absorption spectrum of NO_3 has been analyzed in the visible region (450 to 680 nm) by Johnston and Graham (1974a) who find that the

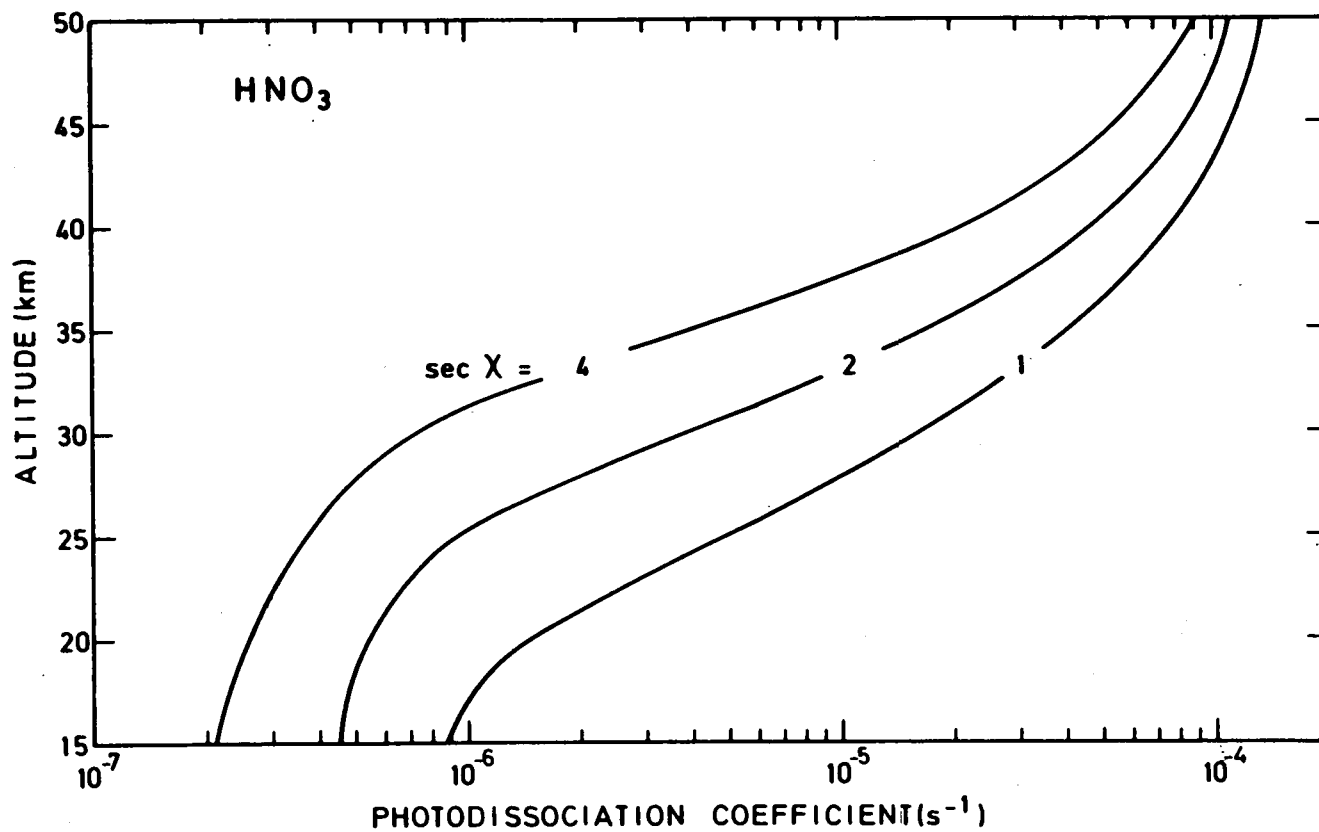


Fig. 36.- Examples of calculated vertical distribution of photodissociation coefficients of nitric acid. Various solar zenith angles χ , $\sec \chi = 1, 2$ and 4 ; (Biaumé, 1973).

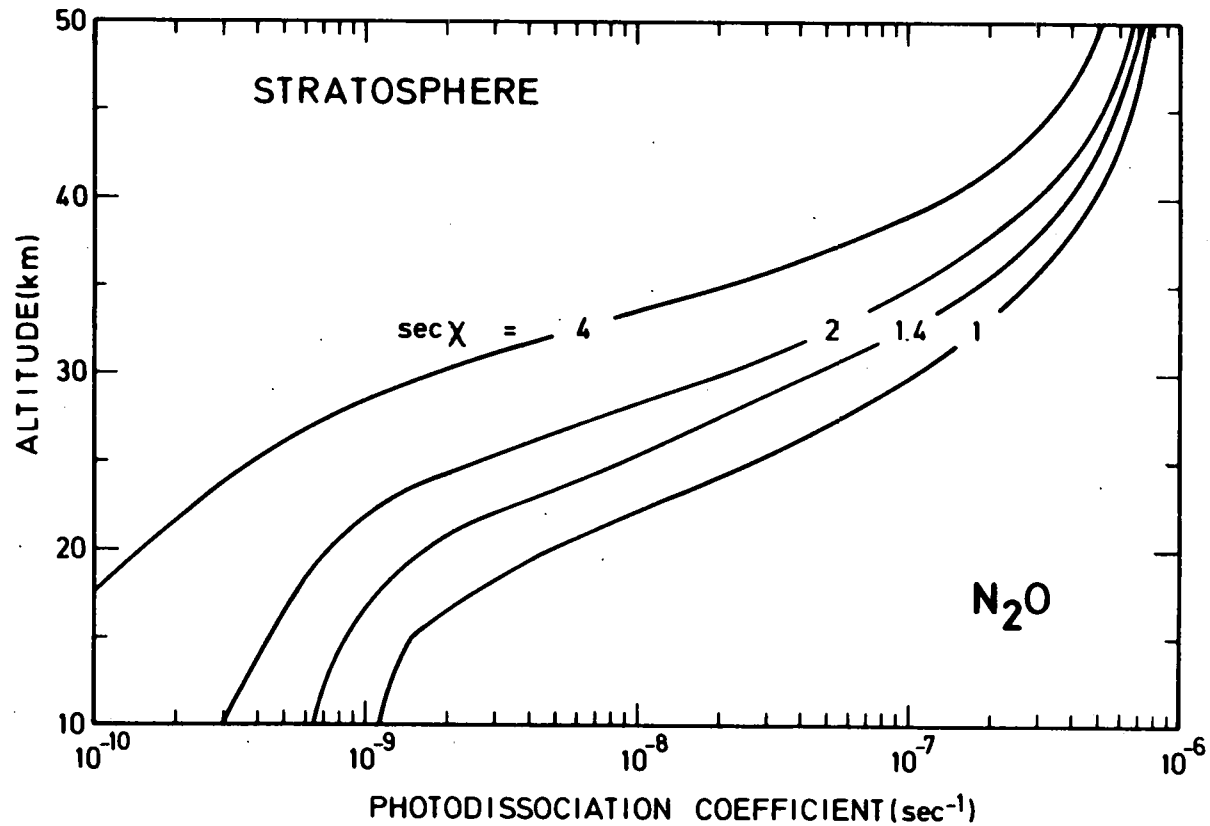


Fig. 37.- Examples of calculated vertical distribution of photodissociation coefficients of nitrous oxide. Various solar zenith angles χ , $\sec \chi = 1, 1.4, 2$ and 4 (Nicolet and Peetermans, 1972).

cross section is between 10^{-19} and 10^{-18} cm^2 . If such an absorption leads to a rapid photodissociation, 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 nm 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 coefficient with altitude (Fig. 36) shows that J_{HNO_3} is not far from 10^{-4} sec^{-1} at the stratopause but that its value decreases rapidly in the stratosphere and reaches less than 10^{-6} sec^{-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 nm and 250 nm and its photodissociation coefficient (Fig. 37) is not greater than 10^{-6} sec^{-1} at the stratopause and reaches only values less than 10^{-9} sec^{-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 $\text{O}(^1\text{D}) + \text{N}_2\text{O}$.

The photodissociation of nitric oxide must be introduced in 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

(0-0) and (1-0) bands near 191 nm 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 $J_{NO} = 2 \times 10^{-6} \text{ sec}^{-1}$ and $8 \times 10^{-7} \text{ sec}^{-1}$ as probable values for overhead sun conditions and a sun altitude of 30° , respectively, at the stratopause level. At the mesopause level, the average value is probably $J_{NO} = 6 \times 10^{-6} \text{ sec}^{-1}$. Such values indicate that a NO molecule is still subject to a photodissociation process in the upper stratosphere.

Finally, the photodissociation of chlorine species, except Cl_2 (eq. 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.

12. FINAL INTRODUCTORY REMARKS

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

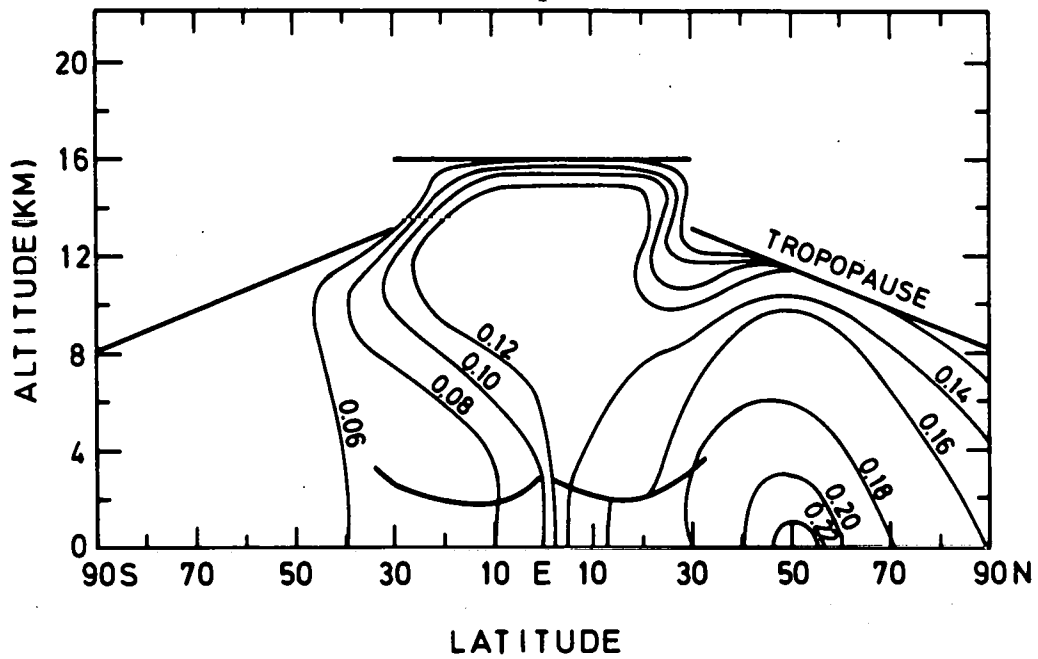


Fig. 38.- Idealized cross section of the distribution of the CO mixing ratio in the troposphere over the Atlantic Ocean, according to Seiler and Schmidt (1974).
Mixing ratio in ppmv.

The cycle of carbon monoxide (Fig. 38) is a first 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 $n(\text{OH})/n(\text{HO}_2)$. 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 action 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

$$\begin{aligned} \frac{dn(\text{O}_3)}{dt} + n(\text{O}_3) [a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2) + b_4 n(\text{NO})] \\ = n(\text{NO}_2) J_{\text{NO}_2} + P(\text{N}) \end{aligned} \quad (206)$$

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 $n(\text{OH})/n(\text{HO}_2)$ and also the absolute values of their concentrations above the stratopause level.

The problem 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 ppmv 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 are small sources 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 C-14 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

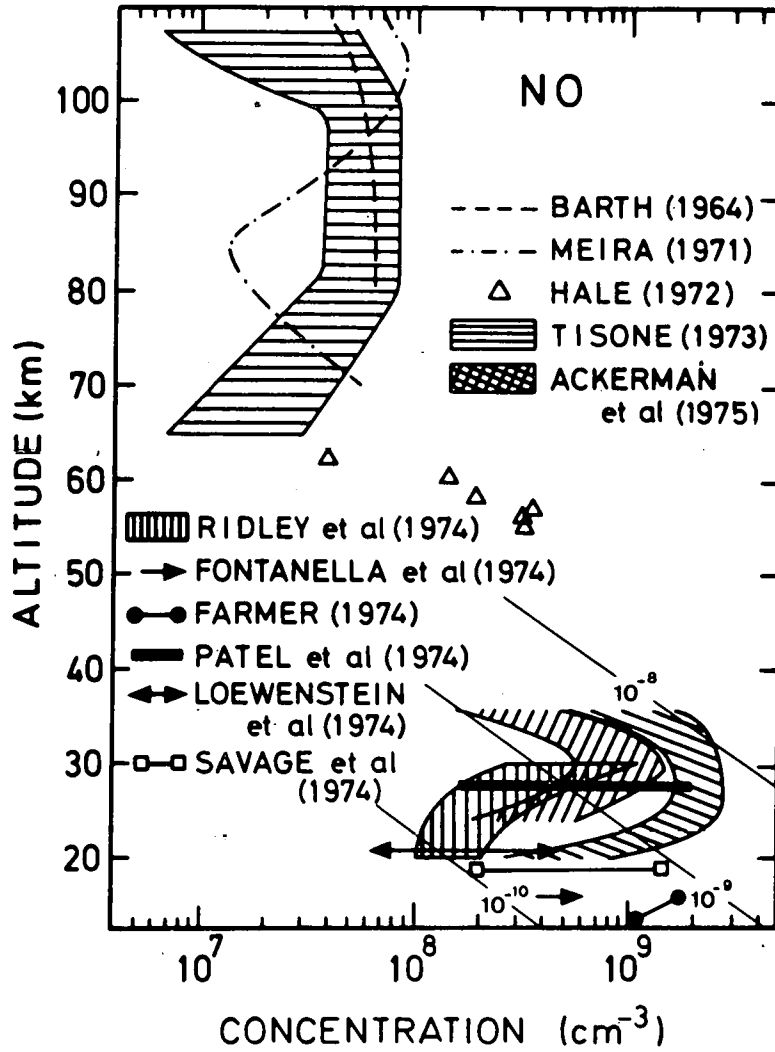


Fig. 39.- Observed nitric oxide concentrations as collected by Ackerman (1975) indicating extremely variable mixing ratios in the stratosphere. All references in Ackerman (1975). 10^{-10} , 10^{-9} and 10^{-8} lines correspond to constant mixing ratios.

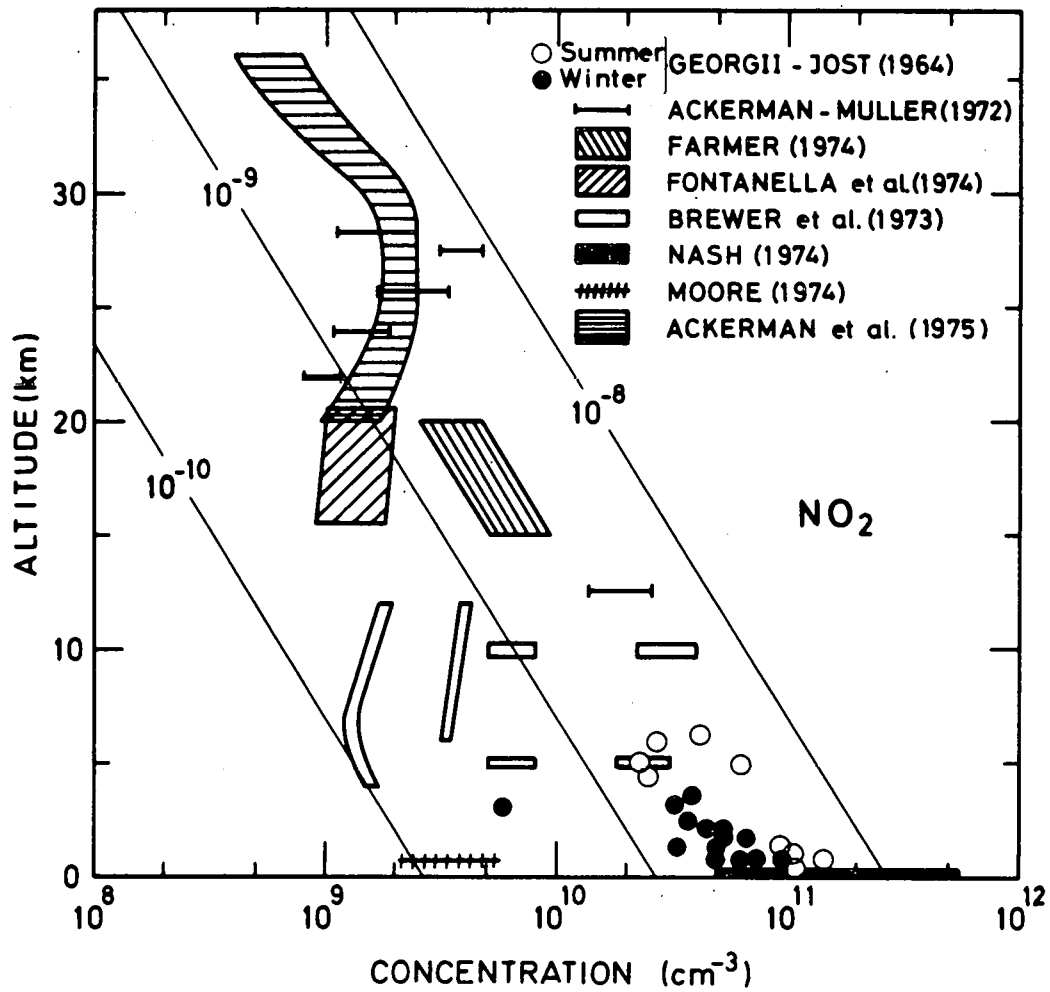


Fig. 40.- Observed nitrogen dioxide concentrations as collected by Ackerman (1975) ; 10^{-10} , 10^{-9} and 10^{-8} correspond to constant mixing ratios.

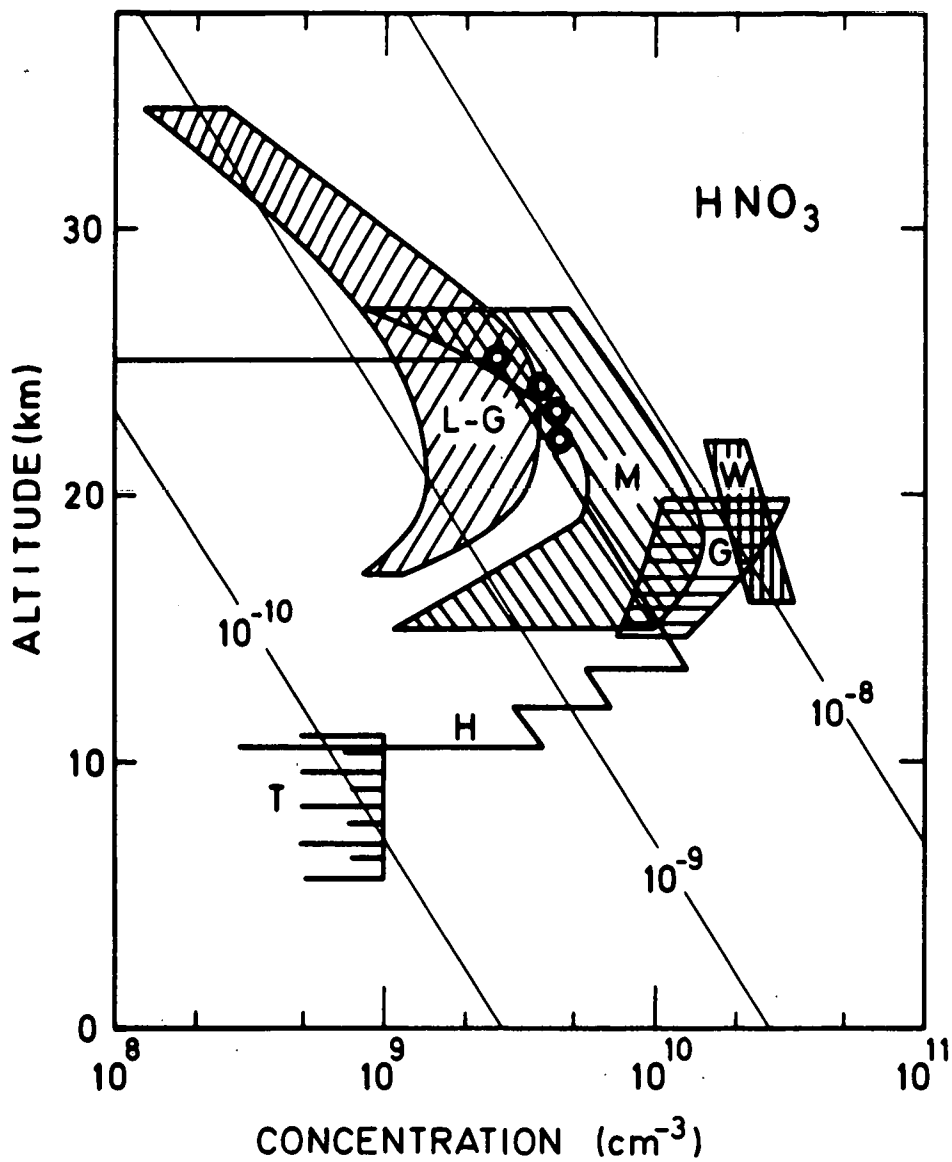


Fig. 41.- Observed nitric acid concentrations as collected by Ackerman (1975). 10^{-10} , 10^{-9} and 10^{-8} lines correspond to constant mixing ratios. L-G, Lazrus and Gandrud (1974); M, Murcray et al., 1974; G, Fontanella et al., 1974; W, Fried and Weinman (1970) and H, Harries et al. (1974). T =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

absolute concentration 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 lands act as source 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 section 6 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 (Fig. 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 Fig. 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 ppbv 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 Fig. 41

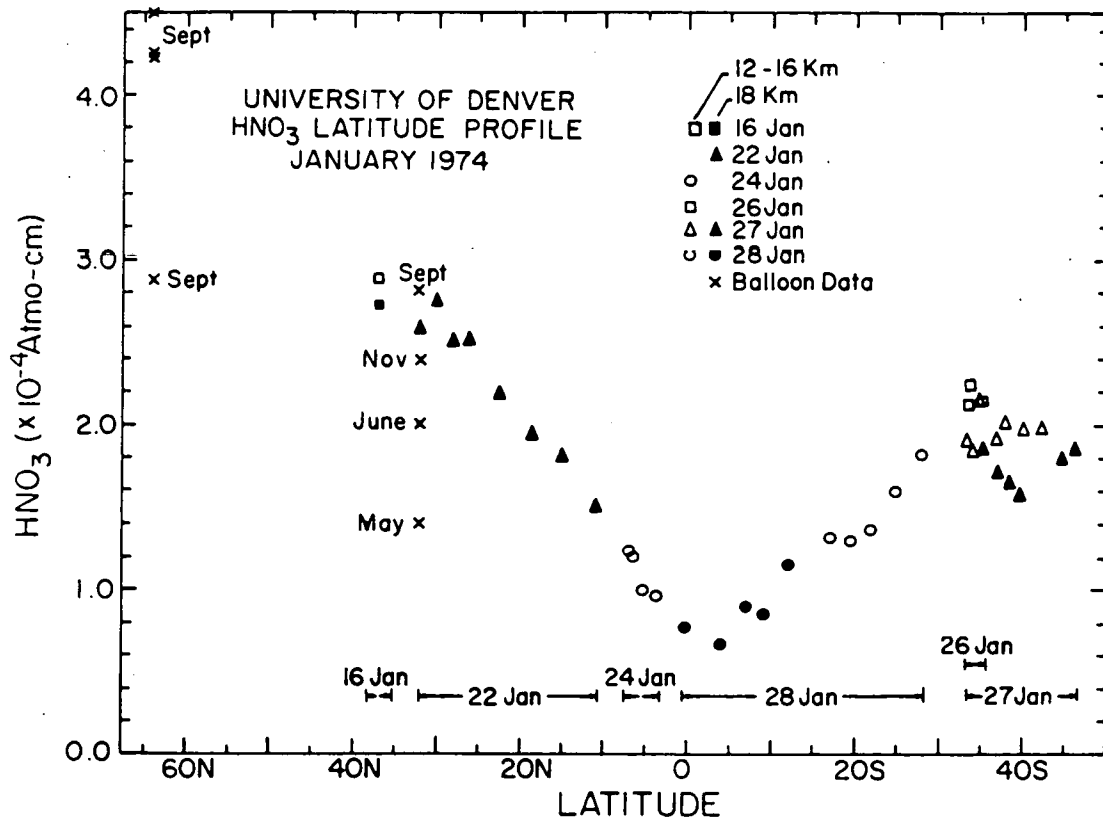


Fig. 42.- Observed (January 1974) nitric acid amount as determined by the University of Denver ; Murcra^y et al. (1975).

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 - 18 km. An example of their results is given in Fig. 42 and shows clearly 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.

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