

CHAPTER 2

A brief overview of stratospheric aeronomy

Marcel NICOLET

Aeronomy Institute, 3 Avenue Circulaire, 1180 Brussels, Belgium

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1. Historical introduction

The aeronomy and meteorology of atmospheric ozone have been studied by many scientists since the suggestion made by Schoenbein (1840a, b) of the existence of an atmospheric constituent having a particular odor (from Greek, *ozein* = to smell). In his letter to Arago, Schoenbein (1840a) wrote as follows: “Etant à peu près sûr que le principe odorant doit être classé au genre de corps auquel appartient le chlore et le brome, c’est-à-dire dans les substances élémentaires et halogènes, je propose de lui donner le nom de *ozone*. Comme je suis convaincu que ce corps se dégage toujours dans l’air en quantité assez notable, lorsque le temps est orageux, je me propose de faire une série d’expériences cette année pour mettre en évidence la présence de l’ozone dans notre atmosphère”.

The exact origin of ozone was deduced by de la Rive (1845) when it was produced in an electrical discharge through pure oxygen. In his letter to Arago, de la Rive (1845) wrote as follows: “Nous avons fait passer à travers un tube un courant d’oxygène parfaitement pur et parfaitement desséché; . . . Ainsi, . . . , l’ozone ne provient que de l’oxygène, et pour en avoir la manifestation, le moyen le plus simple et le plus direct, c’est de faire passer à travers l’oxygène une succession d’étincelles électriques”.

Ozone was chemically proved to exist in the troposphere, at ground level, by Houzeau (1858). However, the first chemical identification was made more than a hundred years ago, by Soret (1863) who, in a Research Note entitled “Sur les relations volumétriques de l’ozone”, wrote “Un grand nombre de chimistes et de physiciens admettent que la molécule d’oxygène ordinaire à l’état gazeux est déjà formée de la réunion de 2 atomes et constitue un oxyde d’oxygène OO . Si l’on adopte cette manière de voir et si l’ozone est un état allotropique de l’oxygène, on est amené à supposer que la molécule d’ozone résulte d’un autre arrangement atomique . . . On pourrait, par exemple, concevoir que 1 molécule

d'ozone fût composée de 3 atomes OOO et constituât un bioxyde d'oxygène”.

The first clear spectroscopic detection of ozone (Chappuis bands) related to the atmosphere was made by Chappuis (1880, 1882). In a Research Note entitled “Sur le spectre d'absorption de l'ozone”, Chappuis (1880) wrote: “Le spectre d'absorption de l'oxygène ozonisé par l'effluve électrique observé à l'aide d'un spectroscopie à un ou deux prismes présente onze bandes obscures bien nettes dans la partie ordinairement visible du spectre. J'ai dressé une carte de ces bandes et je l'ai comparée aux cartes des bandes telluriques”. During the same period, Hartley (1881a) detected in the laboratory the strong ultraviolet spectrum of ozone (Hartley band) below 300 nm. Hartley wrote: “Being much engaged in the examination of organic substances, I delayed the experiments on ozone, until the announcement of the liquefaction of this remarkable body by Messrs Hautefeuille and Chappuis (*Compt. rend.* 91, 522, 1880) attracted my attention once more on the subject”. “The first photograph taken showed a broad absorption-band, stretching from wavelength about 285 to 233 millionths mm”. “The mean wavelength of the rays intercepted by ozone is 256 millionths mm”.

At the same time, Hartley (1881b) made the identification of the atmospheric limit of the solar spectrum detected by Cornu (1878). The conclusions reached by Hartley (1881b) were “that (1) ozone is a normal constituent of the higher atmosphere, (2) it is in larger proportion there than near the earth's surface, (3) the quantity of atmospheric ozone is quite sufficient to account for the limitation of the solar spectrum in the ultraviolet region, without taking into account the possible absorption caused by the great thickness of oxygen and nitrogen”. However, Hartley (1881b) added a fourth conclusion “that the blue tint of the atmosphere is due to ozone”.

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.

Before the first world war, the quantitative analysis of atmospheric ozone was made only by chemical methods at ground level. Among various methods the process introduced by Lévy at Montsouris (Paris) (1896) was in use for 30 years from 1877 to 1907. In

this method the ozone was collected during 24 hours daily and its quantity was estimated by a very elaborated method. But it must be conceded that such observations, even if they are models of accurate work, cannot lead to the true proportion of ozone present in the air, the difficulty being to separate the chemical action of ozone from that of other oxidizing constituents. Nevertheless, it is interesting to know that the average values are 2.5×10^{11} and $1.5 \times 10^{11} \text{ cm}^{-3}$ O_3 molecules cm^{-3} at the maximum in summer (June–July) and at the minimum value in winter (December–January), respectively. The average annual values between 1877 and 1896 vary between $5 \times 10^{10} \text{ cm}^{-3}$ in 1880 and $5 \times 10^{11} \text{ cm}^{-3}$ in 1895. It is not possible to accept all these figures given month after month during 30 years in the *Annuaire de l'Observatoire de Montsouris* as indicating absolute values of the ozone concentration but they can lead to useful comparisons. In any case, they must remind us that in 1865 the French National Academy of Sciences had appointed a special commission of 9 members in order to reduce the number of theoretical, experimental and observational papers on ozone and to receive recommendations and comments before publication. After one hundred years, such a commission could work perhaps on a planetary scale.

2. The period of pioneers of spectroscopic observations

The ozone problem in its general aspects was really developed after the first world war as can be seen from the publication by Fabry (1929) of 27 papers presented at a meeting in Paris which was *de facto* the first international conference on atmospheric ozone.

The first quantitative analysis was made by Fabry and Buisson (1921a, b), in 1920 at Marseille, by a study of the ultraviolet absorption of solar radiation in the Hartley and Huggins bands leading to the first absolute determination of the total atmospheric content with an average value of 0.3 cm (STP) and irregular variations between 0.285 cm and 0.335 cm from 21 May to 23 June. At the same meeting at which as a result of his observational work, Dobson had introduced the real meteorological significance (figs. 1 and 2) of atmospheric ozone (Dobson and Harrison, 1926, 1927; Dobson et al., 1929; Dobson, 1930), Chalonge and Götz (1929) had shown that their daytime and nighttime observations by a

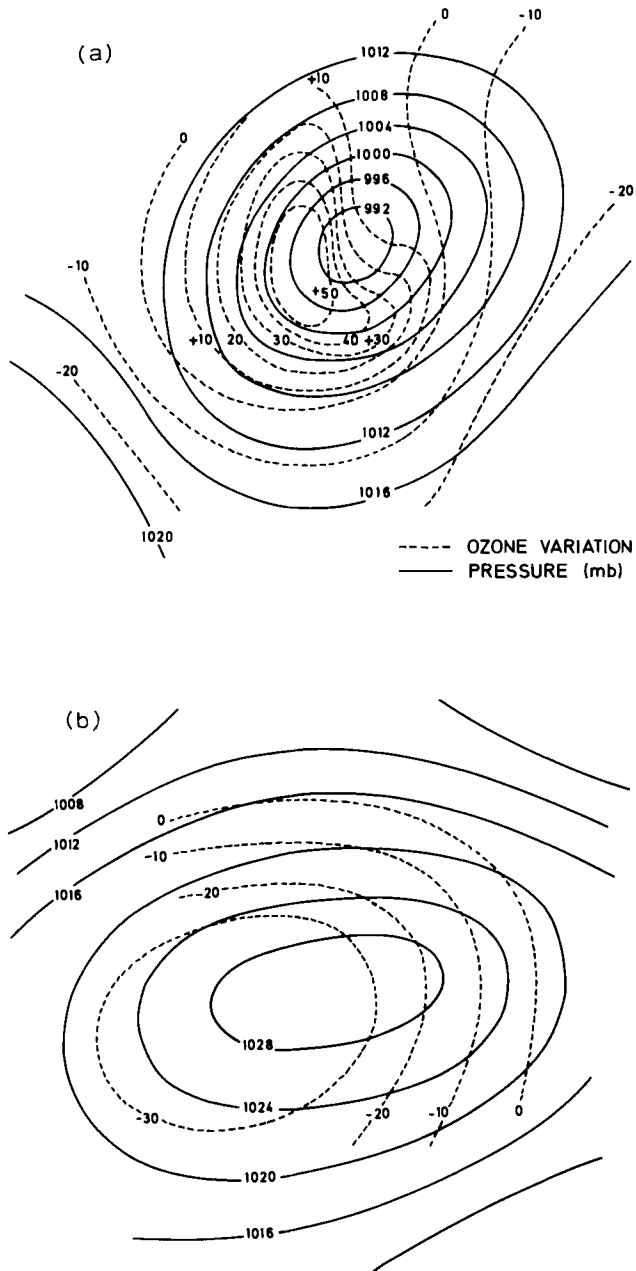


Fig. 1. Typical distribution of increases of total ozone (unit = 0.001 cm at STP) in (a) low-pressure system and (b) high-pressure system as presented in 1929 by Dobson et al. (1929).

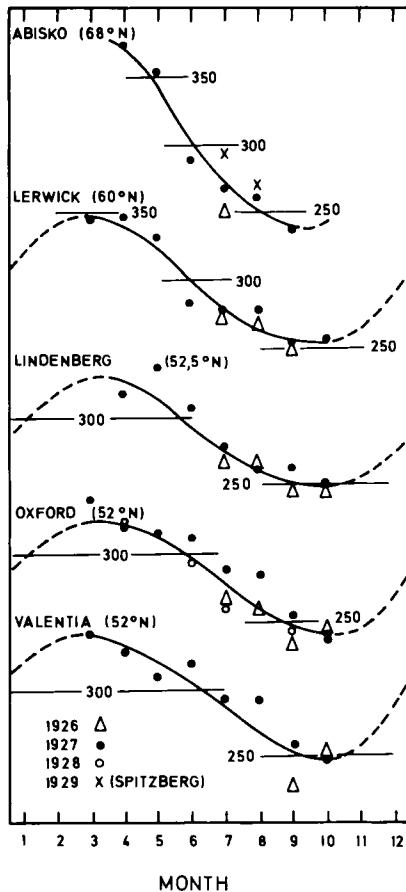


Fig. 2. Seasonal variation of total ozone (unit = 0.001 cm at STP) as detected before 1930 by Dobson (1930). Absolute values correspond to the first calibrations.

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) by Chapman (1930) who had introduced the first aeronomic analysis of the ozone problem. However, in 1929, it was not yet possible to reach a general understanding since the ozone peak (Cabannes and Dufay, 1925, 1927; Götz and Dobson, 1928, 1929) was misplaced at an average height of about 45 km.

The first data on the vertical distribution of stratospheric ozone were obtained by an indirect method introduced by Götz (1931)

during his various observations at Spitzbergen. It is called the Umkehrmethod and was further developed by Götze et al. (1934). The principal results (fig. 3) showed that the average height is only of the order of 25 km and that the main changes in ozone content appear to be centered between 10 and 20 km, a fact of real meteorological significance. Since 1965, the use of chemical instruments (Regener, 1960; Brewer and Milford, 1960) has also been the basis for the first analysis of meridional cross sections of the vertical ozone distribution (see Dütsch, 1969, 1970).

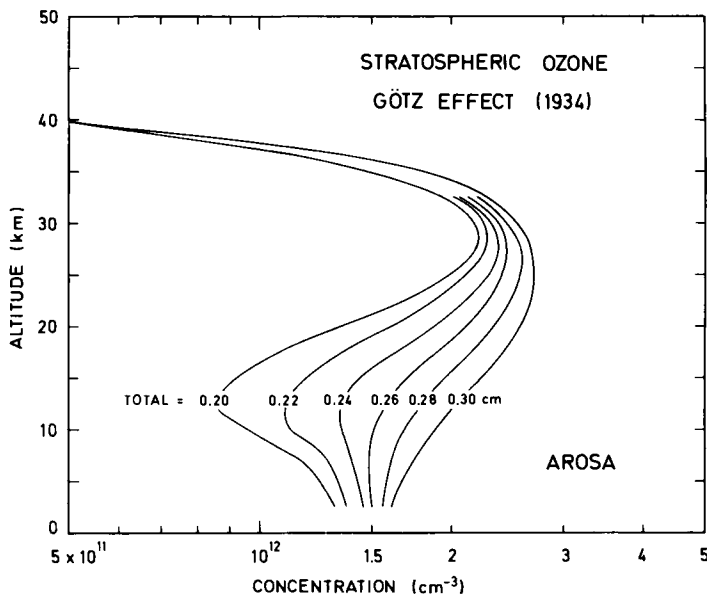


Fig. 3. First determinations of the vertical distribution of stratospheric ozone with the Umkehr method by Götze et al. (1934) where a strong variation is shown below the concentration peak.

3. The present situation

Today, the rocket observations (for example, Krueger, 1973) and also 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 most significant exchanges in 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 standard model cannot represent all atmospheric conditions particularly in the lower stratosphere. The extreme limits reached by the polar tropopause in January in the Northern Hemisphere are about 10° in Africa while the tropical tropopause reaches 40° over the Mediterranean Sea (observations from 1957 to 1965 according to Makhover, 1972). In the summertime, there is an extension of the stratospheric regions with tropical tropopause towards the high latitudes reaching 50° in the Northern Hemisphere. Such differences must be introduced in the study of the behavior of the lower stratosphere when only the mean height of the tropopause is required. However, it is clear that there is a considerable variability which must be considered. An example deduced from a recent analysis by Downie (1974) is illustrated by the various curves of fig. 4 which give, at various latitudes, the number of occurrences of the tropopause height. The scatter is the principal picture of the winter

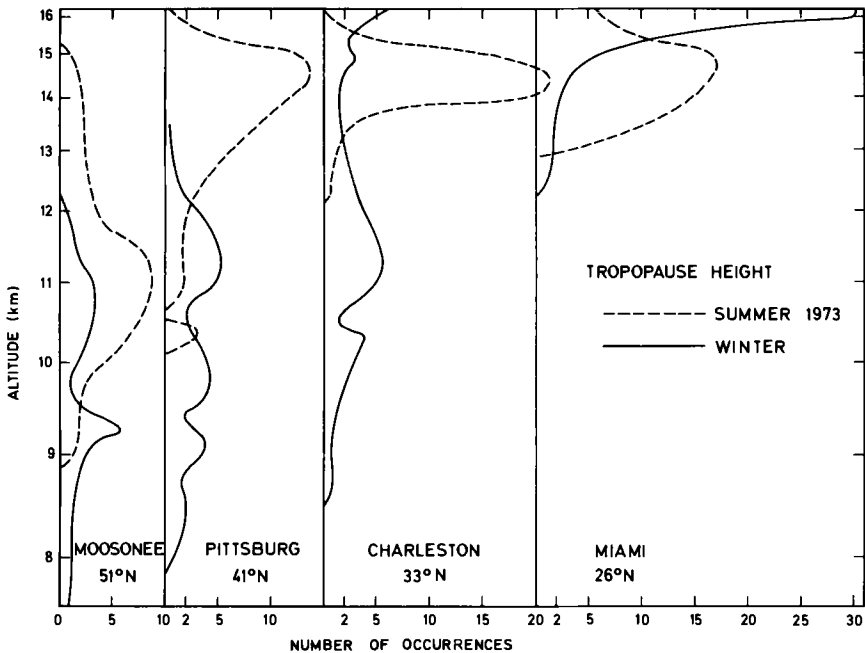


Fig. 4. Variations of tropopause heights for summer and winter conditions at 4 stations between 21° and 51° N, according to Downie (1974).

tropopause for latitudes larger than 30° . The high tropical tropopause (Miami, 26°N) is well defined. Thus, the climatological aspect is not sufficient to assess the atmospheric conditions of the lower stratosphere and it is necessary in many cases to consider synoptic conditions. An indication is given by the vertical cross section illustrated by fig. 5 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 often related to the jet stream by various kinds of transport from simple advection to more complicated dynamic effects.

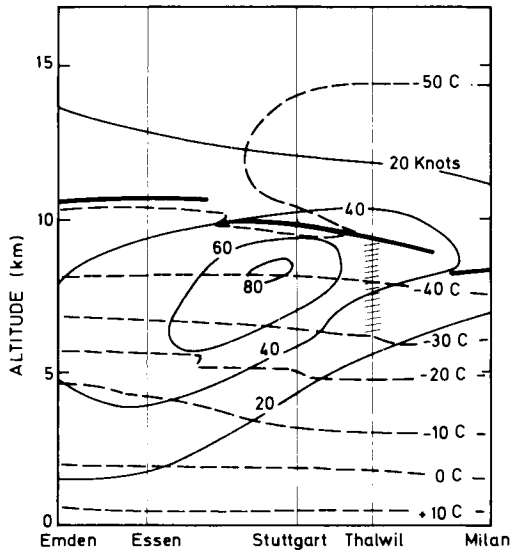


Fig. 5. Vertical profiles from Emden ($53^\circ 4' \text{N}$; $07^\circ 2' \text{E}$) to Thalwil ($47^\circ 3' \text{N}$; $08^\circ 5' \text{E}$) and Milan ($45^\circ 4' \text{N}$; $09^\circ 3' \text{E}$), June 12, 1967 at 12 GMT; from Piaget (1971). Isothermal lines in $^\circ\text{C}$; isopletic lines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

If the variations of the vertical distribution of ozone and its total amount are associated with the tropopause behavior, the seasonal and latitudinal variations are related to more general conditions. 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 by all observations, 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.

An illustration of the ozone production is given in fig. 6 where the annual variation at various latitudes is shown. At the equator, the total production of ozone (or atomic oxygen leading to O_3 formation), which is $(1.4 \pm 0.1) \times 10^{18}$ molecules \cdot cm $^{-2}$ \cdot day $^{-1}$, is practically constant during the year. At 45°, there is a strong annual variation from about 3×10^{17} molecules \cdot cm $^{-2}$ \cdot day $^{-1}$ in January to 1.6×10^{18} molecules \cdot cm $^{-2}$ \cdot 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 a maximum (fig. 7) 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. In any case, the complexity of the ozone vertical distribution in the lower stratosphere indicates the air movement is subject to various kinds of variations that is difficult to introduce in atmospheric models.

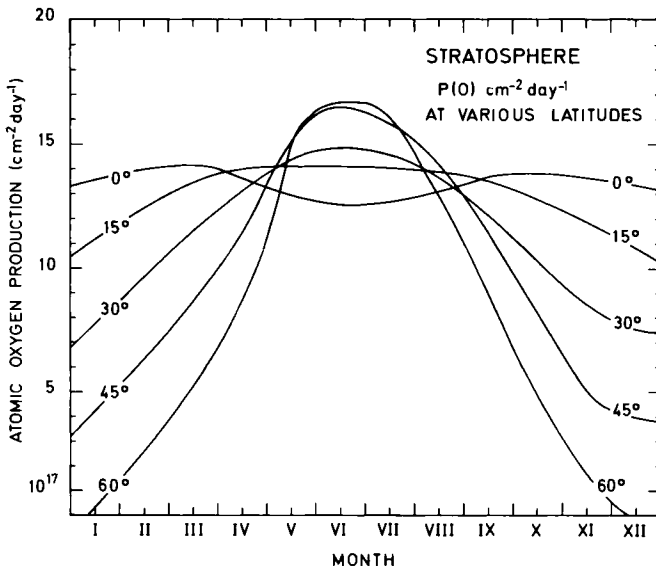


Fig. 6. Annual distribution of ozone production ($\text{cm}^{-2} \cdot \text{day}^{-1}$) at 0°, 15°, 30°, 45° and 60° N.

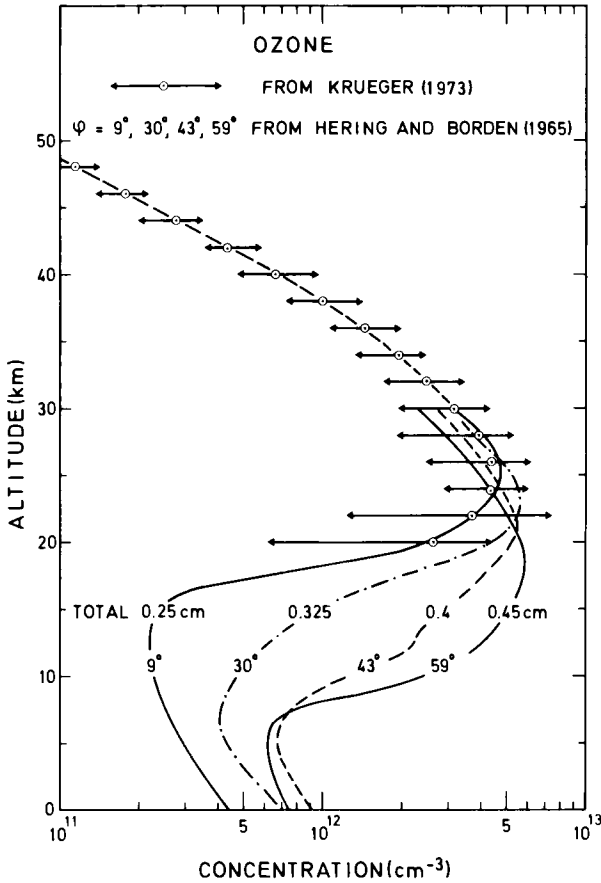


Fig. 7. Average annual values of vertical distribution of ozone concentrations corresponding to an increase of the total amount related to latitude in the lower stratosphere.

4. New developments

The photochemical theory put forward by Chapman (1930, 1943) was first developed for a pure oxygen atmosphere (Mecke, 1931; Wulf and Deming, 1936a, b, 1937; Dütsch, 1946; Craig, 1950) and, therefore, was greatly idealized. However, 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). The problem of methane oxidation requires special attention in the lower stratosphere and the various reactions must be considered in detail (Levy, 1971, 1972, 1973; McConnell et al., 1971; Wofsy et al., 1972; Nicolet and Peetermans, 1973). 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.

Furthermore, stratospheric chlorine has been introduced recently by Stolarski and Cicerone (1974) as a possible sink for ozone. After a preliminary analysis (Crutzen, 1974; Wofsy and McElroy, 1974), its role has been recognized (Clyne and Watson, 1974; Cicerone et al., 1974, 1975a, b; Crutzen, 1974b; Wofsy et al., 1974, 1975a) since its possible action has been demonstrated in

various papers by Molina and Rowland (1974a, b) and Rowland and Molina (1975) in which the effect of industrial 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.

Finally, 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 focused very recently on atmospheric bromine by Wofsy et al. (1975b) since its loss process could be very slow.

5. Ozone formation and destruction

5.1. Oxygen atmosphere

When dissociation of molecular oxygen occurs in the stratosphere (only above 25 km, see fig. 8), the oxygen atoms liberated by

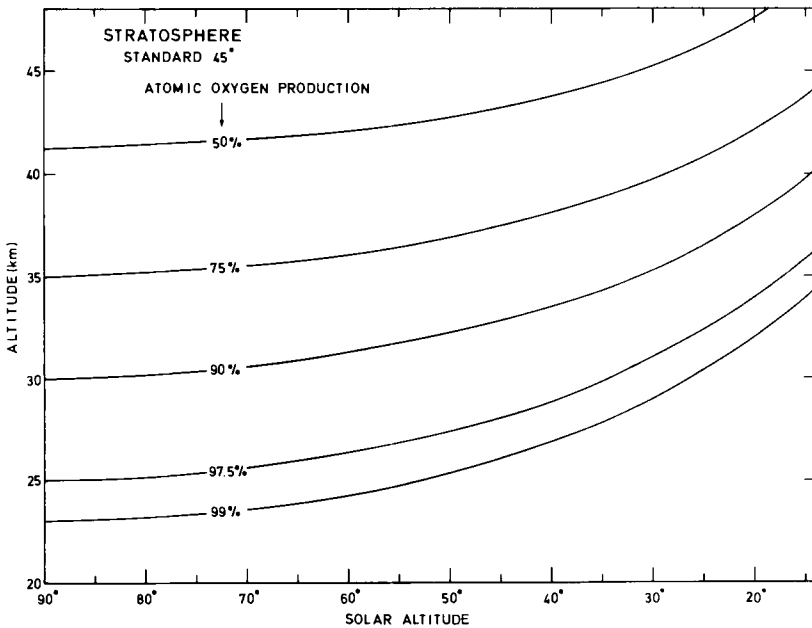
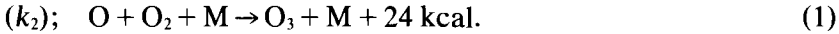


Fig. 8. Total atomic oxygen production (%) for various altitudes of the sun; an overhead sun ($h_{\odot} = 90^{\circ}$) to $h_{\odot} = 20^{\circ}$.

photodissociation unite with oxygen molecules to form ozone by



Ozone molecules can be destroyed by a two-body collision process



Recent laboratory measurements (1971–73) lead for the first time to precise values of k_2 and k_3 which give (see Nicolet, 1975, for references) the following value for the ratio k_2/k_3

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

Before the adopted values were incorrect. For example, Bates and Nicolet (1950c) adopted the ratio k_2/k_3 measured by Eucken and Patat (1936) which gives the following formula

$$k_2/k_3 = 5.5 \times 10^{-25} e^{3070/T} \text{ cm}^3. \quad (3a)$$

After 1960 the following value deduced from an analysis of the thermal decomposition of ozone by Benson and Axworthy (1957) was generally adopted

$$k_2/k_3 = 1.4 \times 10^{-24} e^{-3300/T} \text{ cm}^3. \quad (3b)$$

At the stratopause level ($T = 273 \text{ K}$), the ozone concentrations which can be deduced from (3a), (3b) and (3) are in the following proportions 2.05, 5.20 and 4.12, respectively. This indicates that the photochemical equilibrium concentration $n_*(\text{O}_3)$ which can be used in the upper part of the stratosphere and certainly at the stratopause had not been determined exactly before 1970.

The photodissociation coefficients of O_2 and O_3 being J_2 and J_3 respectively,

$$n_*(\text{O}_3) = \frac{k_2}{k_3} n(\text{M}) n^2(\text{O}_2) \frac{J_2}{J_3} \quad (4)$$

was not correctly determined, with the values of Eucken and Patat (1936) leading almost to the observed values of $n(\text{O}_3)$. With the correct values of k_2 and k_3 it is not possible to reach an agreement between the calculated values and the observed values when the ozone problem is considered in a pure oxygen atmosphere. The theoretical values are about twice the observed values.

Since the various parameters introduced in (4) cannot be changed by a factor of the order of 4, there are only aeronomic

possibilities corresponding to an increase of the effective value of J_3 due to various actions of HO_x , NO_x , ClO_x , BrO_x ,

5.2. Hydrogen–oxygen atmosphere

A hydrogen–oxygen atmosphere seems to be very complicated when all reactions are considered (Bates and Nicolet, 1950c). However, it is possible to deduce (in the stratosphere) the action of the principal reactions when a simple reaction scheme as indicated in fig. 9 is used. At the stratopause a direct effect on atomic oxygen

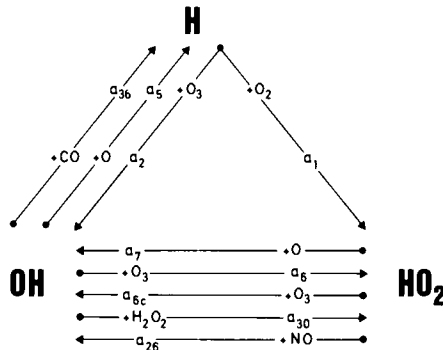


Fig. 9. Simple reaction scheme of H, OH and HO_2 showing their interconnection in the stratosphere a_1 , a_2 , a_5 and a_7 at the stratopause, a_6 and a_{6c} in the mean and lower stratosphere, a_{26} and a_{36} at the tropopause.

is important (a_5 and a_7) and in the lower stratosphere the effect on ozone (a_6 and a_{6c}) must be considered. Instead of (4), we may write

$$n_*^2(\text{O}_3) = \frac{k_2}{k_3} n(\text{M}) n^2(\text{O}_2) \frac{J_2}{J_3(1 + A)} \quad (4a)$$

where A is the correction factor.

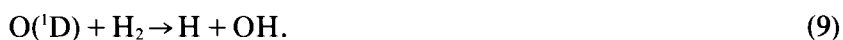
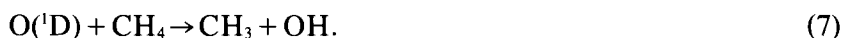
$$A = \frac{a_5 n(\text{OH}) + a_7 n(\text{HO}_2)}{2k_3 n(\text{O}_3)} \quad (5a)$$

Experimental determination of a_5 and a_7 (not yet measured) are required and exact values of $n(\text{OH})$ and $n(\text{HO}_2)$ are needed. Thus, the correction term (5a) shows clearly that it is difficult to make an exact numerical application of the effect of hydroxyl and hydroperoxyl radicals on the ozone concentrations 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 concentrations at the stratopause level requires that their concentrations be of the order of 10^7 cm^3 . At 40 km, it seems that OH and HO₂ cannot have an important effect, but NO₂ can play a role.

In the lower stratosphere, the problem is not yet resolved. Instead of the simple reaction scheme shown in fig. 9, the effect of CO and NO must be introduced in the lower stratosphere.

Nevertheless, the production of OH and HO₂ radicals depend on the dissociation of H₂O, CH₄ and H₂ which occur through the following reactions



Important reactions such as



lead to the re-formation of water vapor in the stratosphere. Methane is destroyed by reaction (8) and is replaced in the stratosphere and mesosphere by transport from the troposphere. As far as H₂ is concerned, it is subject to various reactions for which the rate coefficients are not well known (see details, Nicolet, 1975). Before final conclusions can be reached, absolute values of the OH and HO₂ concentrations must be determined and laboratory measurements of several rate coefficients are still needed. Methane must be introduced since it leads to the formation of stratospheric water vapor and with molecular hydrogen may lead to the complete understanding of stratospheric aeronomic processes.

5.3. *Nitrogen–hydrogen–oxygen atmosphere*

The presence of nitrogen oxides in the upper atmosphere requires the production of atomic nitrogen (Nicolet, 1945, 1965a, b; Bates, 1952) or the dissociation of nitrous oxide (Bates and Witherspoon,

1952; Bates and Hays, 1967). This problem was developed by Nicolet (1955a, b) in relation to the airglow. In the ionospheric regions, ionic reactions lead to excited atoms $N(^2D)$ (Norton and Barth, 1970; Strobel et al., 1970; Nicolet, 1970b; Strobel, 1971a, b) which react rapidly with O_2 to form nitric oxide molecules. In the stratosphere, the reaction of the electronically excited oxygen atom $O(^1D)$ with N_2O (Nicolet, 1971) has been considered as an important source of nitric oxide (Nicolet and Vergison, 1971; Crutzen, 1971; McElroy and McConnell, 1971; Nicolet and Peetermans, 1972; Johnston, 1972). Cosmic rays (Warneck, 1972; Nicolet and Peetermans, 1972; 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.

Two bimolecular processes must be considered as essential aeronomic processes playing a role in the destruction of ozone. One is the reaction with oxygen atoms.



and the other reaction of nitric oxide with ozone



is followed in a sunlit atmosphere by



Since the lifetime in the solar radiation field of NO_2 molecules is $100 < \tau_{\text{NO}_2} < 200$ seconds, a photoequilibrium exists and, in the stratosphere, may lead to

$$n(\text{NO}_2)/n(\text{NO}) = b_4 n(\text{O}_3)/J_{\text{NO}_2}. \quad (14)$$

The scheme of the principal reactions related to the photochemistry of $\text{O}-\text{O}_3$ with H , OH and HO_2 and with NO and NO_2 is given in

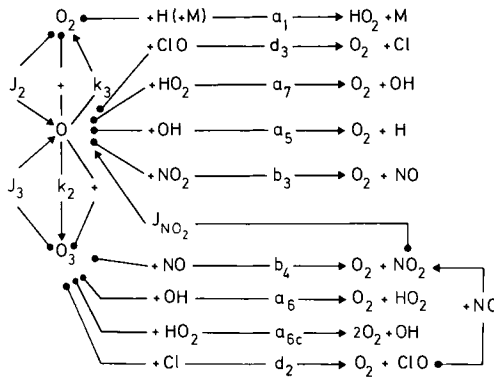


Fig. 10. Stratospheric reactions occurring in a nitrogen-oxygen atmosphere that are related to the production and loss of odd oxygen. Effects of chlorine compounds are also indicated to show the general scheme in which are simultaneously involved the chlorine, nitrogen and hydrogen radicals. Bromine action is identical to that of chlorine.

fig. 10 and corresponds to the following equation

$$\begin{aligned} \frac{dn(\text{O}_3)}{dt} + n(\text{O}_3)[a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2)] \\ + n(\text{O})[2k_3 n(\text{O}_3) + a_5 n(\text{OH}) + a_7 n(\text{HO}_2) + 2b_3 n(\text{NO}_2)] = 2n(\text{O}_2)J_2 \end{aligned} \quad (15)$$

which shows that the correction term in eq. (4a) at the stratopause

level becomes

$$A = \frac{a_5n(\text{OH}) + a_7n(\text{HO}_2) + 2b_3n(\text{NO}_2)}{2k_3n(\text{O}_3)}. \quad (5b)$$

Thus, it can be concluded that the action of nitrogen oxide on stratospheric ozone depends on the vertical distribution and absolute concentration of nitrogen dioxide.

However, the whole chemistry of nitrogen oxides, namely the reactions leading to the formation and destruction of NO, NO₂, NO₃, HNO₂, HNO₃, N₂O₅, . . . must be introduced. The final loss process must correspond to the transport of nitric acid from the stratosphere into the troposphere where it is soluble in water. The action of advection and various dynamic processes at the tropopause level may modify the lower boundary conditions which affect the vertical distribution of nitrogen oxides in the stratosphere.

5.4. 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, CFCl₃, and of the dichlorodifluoromethane, CF₂Cl₂, which are observed in the troposphere (CFCl₃, Lovelock, 1971, 1972; Lovelock et al., 1973; Wilkniss et al., 1973; Lovelock, 1974; Wilkniss et al., 1975a; CFCl₃ and CF₂Cl₂, 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, CCl₄, 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 also

photodissociated in the stratosphere and could play therefore a role in the destruction of stratospheric ozone.

Examples of atmospheric concentrations determined by Grimrud and Rasmussen (1975) from measurements made in the rural Northwest of Washington State (USA) between December 1974 and February 1975 are:

Dichlorodifluoromethane	CF_2Cl_2	230 ± 10 ppt
Trichlorofluoromethane	CFCl_3	128 ± 8
Carbon tetrachloride	CCl_4	120 ± 15

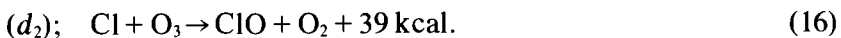
The atmosphere contains also small quantities of other halocarbons such as $\text{C}_2\text{H}_3\text{Cl}_3$, C_2Cl_4 , CHCl_3 , The relative concentration given by Grimsrud and Rasmussen (1975) are

Methylchloroform	$\text{C}_2\text{H}_3\text{Cl}_3$	100 ± 15 ppt
Tetrachloroethylene	C_2Cl_4	20 ± 10
Chloroform	CHCl_3	20 ± 10

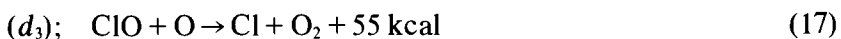
Atmospheric chloroform has been recently discussed by Yung et al. (1975) who have defined the magnitude and identified the nature of the source for this industrial compound.

Finally, the action of methyl chloride, CH_3Cl , has been introduced very recently by Cicerone et al. (1975) and must be considered at the present as the principal halocarbon of the atmosphere since its natural concentration is relatively high. Methyl chloride seems to be the result of the marine biological activity. Grimrud and Rasmussen (1975) have reported a relative concentration of $5.3 \pm 3 \times 10^{-10}$ in the USA and Lovelock (1975) gives at Bowerchalke, Southern England from December 1974 until April 1975 a mean concentration of 1.1×10^{-9} .

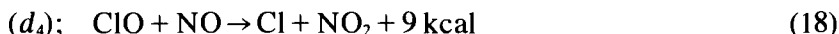
The problem of chlorine species in the stratosphere begins, after their transport from the troposphere, by their photodissociation in the ozonosphere or their destruction by reaction with OH and O('D). After the various dissociation processes, we must consider the reaction of a chlorine atom with ozone which leads to chlorine monoxide



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

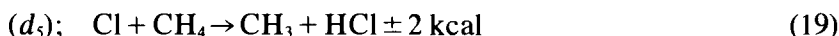


and

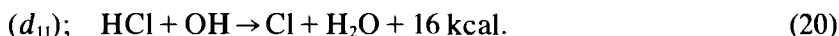


which is followed in a sunlit atmosphere by (13), $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$.

When a chlorine atom is produced, it may also react by bimolecular reactions with various stratospheric molecules such as CH_4 , H_2 , HO_2 , H_2O_2 and HNO_3 . The most important reaction is



which can be followed by



Hydrogen chlorine, which should lead to the normal loss process of stratospheric chlorine, cannot attain a steady state in the stratosphere since transport is involved at the lower boundary (tropopause) even if it is not too far from day equilibrium conditions at the stratopause.

The catalytic removal of ozone by chlorine compounds (fig. 10) occur by the direct action of reaction (16) and by the indirect action of reaction (17) which may be counterbalanced at lower levels by (18). A concentration of chlorine atoms of the order of $5 \times 10^5 \text{ cm}^{-3}$ would lead to a loss rate of $2 \times 10^{-5} n(\text{O}_3) \text{ cm}^{-3} \cdot \text{sec}^{-1}$; a Cl concentration of about 10^4 cm^{-3} would lead to a lifetime of an ozone molecule of the order of a year. In the lower stratosphere (below the ozone peak) the action of chlorine compounds is related to the production term $d_4 n(\text{NO})n(\text{ClO})$, that is, depends on the simultaneous opposite actions of ClO reacting with O or with NO.

In conclusion, if the mixing ratio of odd chlorine atoms tends to reach 10^{-9} , a very precise analysis is required since the efficiency for ozone depletion by the mechanism (16), $d_2 n(\text{Cl})n(\text{O}_3) \text{ cm}^{-3} \cdot \text{sec}^{-1}$ must be considered in the upper stratosphere ($> 35 \text{ km}$) where the mechanism (18), $d_4 n(\text{ClO})n(\text{NO}) \text{ cm}^3 \cdot \text{sec}^{-1}$ cannot be considered as an ozone production term. A Cl concentration greater than $5 \times 10^4 \text{ cm}^{-3}$ and reaching 10^5 cm^{-3} would lead to ozone removal according to the mechanism (16) $2d_2 n(\text{Cl})n(\text{O}_3) \text{ cm}^{-3} \cdot \text{sec}^{-1}$ which will compete with the mechanisms (11), $2b_3 n(\text{O})n(\text{NO}_2)$ and (5a), $2a_5 n(\text{O})n(\text{OH})$ in the upper stratosphere and at the stratopause level, respectively.

In any case, Crutzen and Isaksen (1975) have claimed that at the present time, there is a reduction in total ozone of about 2% due to CFCl_3 , CF_2Cl_2 , CCl_4 and $\text{C}_2\text{H}_3\text{Cl}_3$ and of about 1% due to CH_3Cl . Such results are deduced from a theoretical model as given by the authors.

5.5. Bromine compounds

The chemistry of stratospheric bromine (Wofsy et al., 1975) follows the chemistry of stratospheric chlorine (fig. 10) as far as the ozone–oxygen aeronomic reactions are concerned. Atomic bromine reacts with ozone



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



and



But a bromine atom does not react with CH_4 and H_2 , but perhaps with HO_2 and H_2O_2



which can be followed by



According to Wofsy et al. (1975), the flux of inorganic bromine at ground level would be of the order of 5×10^7 molecules $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ and of CH_3Br of 3×10^6 $\text{cm}^{-2} \cdot \text{sec}^{-1}$ in order to agree with the observations by Lazrus et al. (1975) which indicate relative concentrations of stratospheric bromine of the order of 10^{-11} . Such a concentration would lead according to Wofsy et al. (1975) to a reduction of approximately 0.3% of the global budget of O_3 . Such a result is deduced from a theoretical model which is defined by the authors.

6. Conclusion

It seems that it is now possible to resolve the theoretical problem of stratospheric ozone since the correct aeronomic equations are known and the principal atmospheric parameters can be used. However, it is not yet possible to determine with enough precision the behavior of certain minor constituents, particularly when all their sources and sinks are not known. It is clear that additional observational and experimental studies are still required for a complete aeronomic discussion of industrial or natural halocarbons. But other problems are not yet resolved.

The cycle of carbon monoxide 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.

The problem of the role of OH and HO_2 radicals as studied by Warneck (1974, 1975) or observed by Wang et al. (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 CH₄ and formaldehyde photodissociation in the stratosphere are small sources of H₂ 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 H₂O 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 CH₄. At the same time the atmospheric CH₄ 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 N₂O molecules is due to a photodissociation process. The vertical distribution of its absolute concentration in the upper stratosphere should be known at various latitudes since N₂O 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 above 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 observational results (for example Ackerman, 1975) we can see 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) 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 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. Their results show 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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