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Chemical kinetics in the stratosphere

by

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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

This paper has been presented at the AGARD meeting on "Atmospheric Pollution by Aircraft Engines" held in London, April 9-13, 1973. It will be published in the conference proceedings.

AVANT-PROPOS

Ce texte a été présenté à la 41ème réunion du groupe de travail "propulsion et énergétique" de l'AGARD qui s'est tenu à Londres du 9 au 13 avril 1973 et qui avait pour thème "la pollution atmosphérique par les moteurs d'avions". Cette communication sera publiée dans le compte rendu de la réunion.

VOORWOORD

Deze tekst werd voorgedragen tijdens de "AGARD meeting on Atmospheric Pollution by Aircraft Engines", 9-13 April 1973, te Londen. Hij zal in the "Conference Proceedings" uitgegeven worden.

VORWORT

Dieser Text wurde zum "AGARD meeting on Atmospheric Pollution by Aircraft Engines", 9-13 April 1973, in London vorgestellt. Er wird in den "Conference Proceedings" herausgegeben werden.

CHEMICAL KINETICS IN THE STRATOSPHERE

by

G. BRASSEUR

Summary

Ozone is produced by the photodissociation of molecular oxygen and can be destroyed by several reactions involving the nitrogen - hydrogen - oxygen atmosphere. In the lower part of the stratosphere and for photochemical conditions, an important loss of ozone is due to the NO_x reactions. Nitric oxide is formed in the stratosphere after dissociation of nitrous oxide by the excited oxygen atom $\text{O}(^1\text{D})$. The formation of nitric acid is possible by the presence of hydroxyl radicals. Therefore a careful study of the hydrogen atmosphere is necessary. Water vapor, methane and molecular hydrogen have an indirect influence on the ozone distribution in the stratosphere.

Résumé

L'ozone est formé à partir de la photodissociation de l'oxygène moléculaire et peut être détruit par différentes réactions faisant intervenir l'atmosphère d'oxygène - hydrogène et azote. Dans la partie inférieure de la stratosphère et pour des conditions photochimiques, les oxydes d'azote jouent un rôle important dans la destruction de l'ozone. Le monoxyde d'azote est formé par la dissociation de l'hémioxyde d'azote par l'atome d'oxygène dans son état excité ^1D . La formation d'acide nitrique est possible par la présence de radicaux hydroxyls. Une étude précise de l'atmosphère d'hydrogène s'impose donc. La vapeur d'eau, le méthane et l'hydrogène moléculaire ont une influence indirecte sur la distribution de l'ozone stratosphérique.

Samenvatting

Ozon wordt gevormd door fotodissociatie en kan vernietigd worden door verscheidene reacties in de stikstof - waterstof - zuurstof atmosfeer. In de lagere stratosfeer en onder welbepaalde fotochemische voorwaarden is een belangrijk verlies van Ozon te wijten aan de NO_x reacties. NO wordt gevormd in de stratosfeer na disassociatie van N_2O door het geëxciteerde zuurstof atoom $\text{O}(^1\text{D})$. De vorming van HNO_3 is mogelijk wegens de aanwezigheid van de hydroxyl radicalen. Een omzichtige studie van de waterstof atmosfeer is dan ook noodzakelijk. Waterdamp, methaan en moleculaire waterstof hebben een onrechtstreekse invloed op de ozon verdeling in de stratosfeer.

Zusammenfassung

Ozon wird durch die Photodissoziation molekularen Sauerstoffes produziert und kann durch verschiedene Reaktionen, die die Stickstoff - Wasserstoff - und Sauerstoffatmosphäre dazwischenkommen lassen. In dem niederen Teil der Stratosphäre und bei photochemischen Bedingungen wird ein Verlust an Ozon von NO_x Reaktionen veranlasst. Stickstoffoxyd wird in der Stratosphäre gebildet nach der Dissoziation des Stickoxyduls durch das angeregte Sauerstoffatom. Die Bildung Stickstoffoxyds ist möglich durch dem Vorhandensein Hydroxylradikale. Deswegen ist eine genaue Studie der Wasserstoffatmosphäre notwendig. Wasserdampf, Methan und molekularer Wasserstoff haben einen mittelbaren Einfluss auf die Ozonverteilung in der Stratosphäre.

1. INTRODUCTION

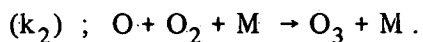
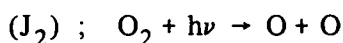
The aeronomy of the stratosphere has been studied with much attention for many years by different authors (see for ex. Nicolet [1], [2], [3]) but an increased attention has been given to these problems since it has been pointed out that high altitude aircrafts could have an impact on the earth's climate and on the U.V. radiation intensity at ground level.

Before trying to estimate the magnitude of such impacts, it is necessary to clearly understand the physical processes of the natural stratosphere. Many important questions still remain unsolved, e.g. transport mechanisms, specially through the tropopause; important reaction rates and absorption cross sections are not known with enough accuracy.

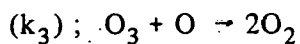
The purpose of this paper is to show that the problem of the stratosphere can not be solved without a good understanding of its photochemistry and the introduction of most minor constituents. A special attention will be devoted to the nitrogen oxides chemistry.

2. PRODUCTION AND DESTRUCTION OF OZONE

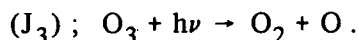
The minor constituent which plays the major role in the stratosphere certainly is ozone which is produced from the photodissociation of molecular oxygen for radiation of wavelength shorter than 242 nm :



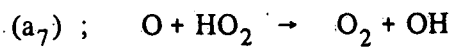
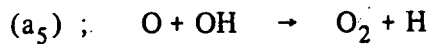
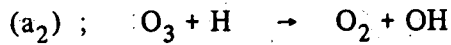
It is destroyed by reaction



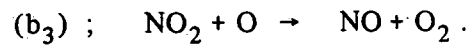
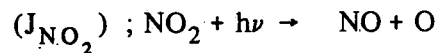
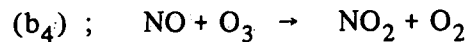
or by photodissociation



These reactions have been proposed in 1930 by Chapman [4] and explain the presence of a maximum of the ozone concentration in the middle of the stratosphere. But the obtained concentrations are too high compared with most experimental data since other loss processes have been omitted. In the upper stratosphere and above the stratopause, odd oxygen is destroyed by hydrogen compounds (Bates and Nicolet [5]).



and in the lower stratosphere by the NO_x catalytic cycle (Crutzen [6], Johnston [7])



The production rate of ozone is thus given by

$$P(O_3) = 2 J_2 n(O_2)$$

and is represented on fig. 1 for an overhead sun. Its integrated value between 10 and 50 km is of the order of $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ but slightly varies with latitude and season since the penetration of solar radiation depends on the ozone content which is larger in the polar regions than near the equator.

The loss rates of ozone are respectively given for the Chapman reactions by

$$L_1(O_3) = \frac{2 J_3 k_3 n^2(O_3)}{k_2 n(M) n(O_2)}$$

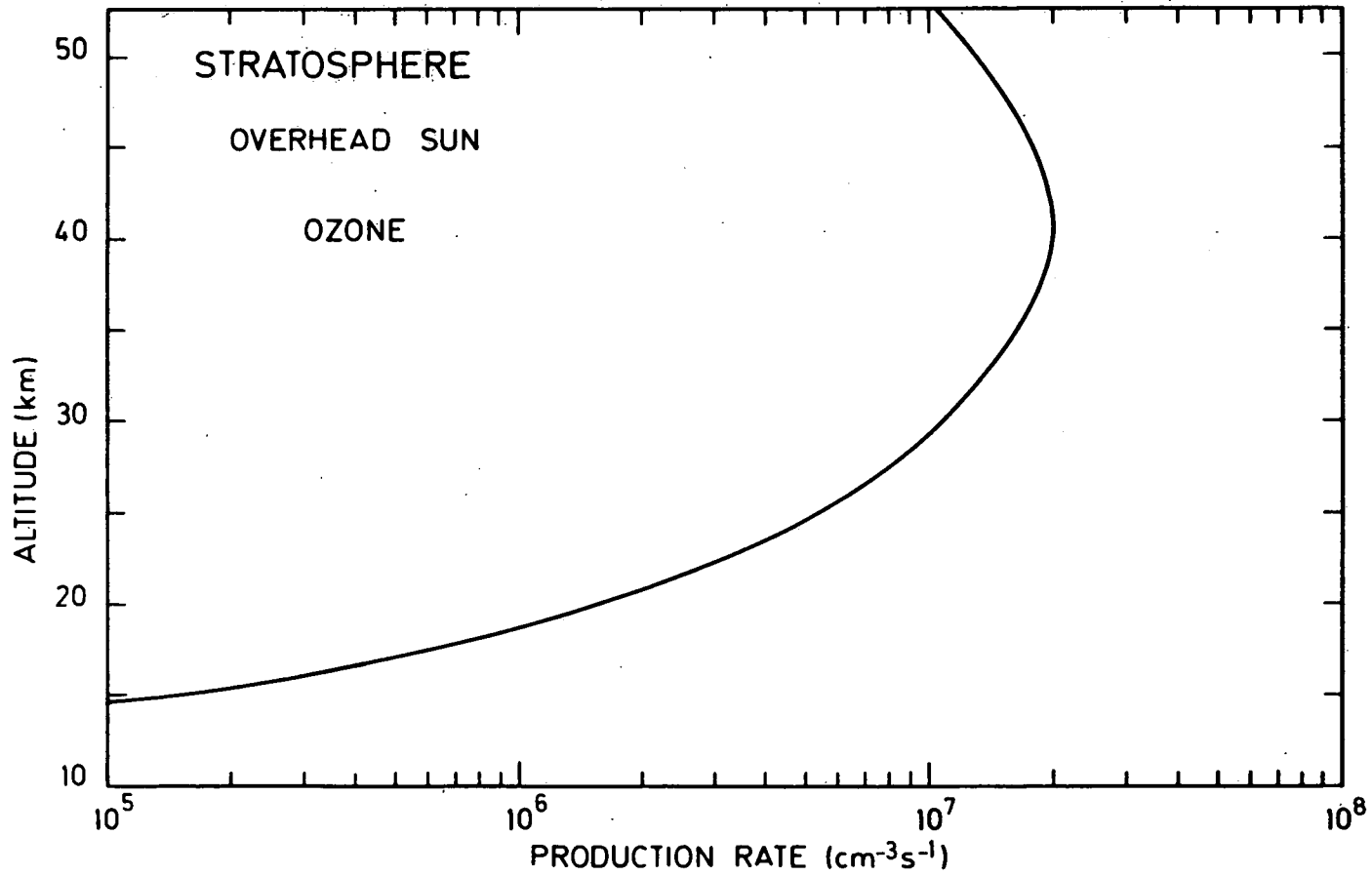


Fig. 1.- Production rate of odd oxygen for an overhead sun.

for the hydrogen compounds reactions by

$$L_2(O_3) = \frac{J_3 n(O_3)}{k_2 n(M) n(O_2)} [a_5 n(OH) + a_7 n(HO_2)] + a_2 n(H) n(O_3)$$

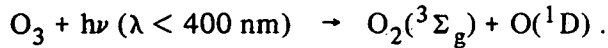
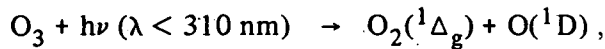
and for the NO_x reactions by

$$L_3(O_3) = \frac{2 J_3 b_3 n(NO_2) n(O_3)}{k_2 n(M) n(O_2)}$$

The loss rates L₁ and L₃ are represented on fig. 2 for mid-latitude conditions and using respectively 10⁻⁹ and 3 x 10⁻⁹ as NO₂ mixing ratio. Rate L₂ has not been represented since the rate constants a₅ and a₇ and the HO_x distributions are not well known. Nevertheless, order of magnitude calculations shows that L₂ can be neglected in the major part of the stratosphere compared with L₁ and L₃. The integrated loss between 10 and 50 km gives for L₁ 1.7 x 10¹³ cm⁻² s⁻¹ and for L₂ 6 x 10¹² cm⁻² s⁻¹ and 1.8 x 10¹³ cm⁻² s⁻¹ if 10⁻⁹ and 3 x 10⁻⁹ are used again for the NO₂ mixing ratio.

3. THE HO_x CHEMISTRY IN THE STRATOSPHERE.

The production of oxygen atoms in their electronically excited ¹D state plays an important role in the stratospheric aeronomy.



A precise determination of the O(¹D) distribution depends on the quantum yield of these processes. According to DeMore and Raper [8] the quantum efficiency at λ < 310 nm is equal to unity and it sharply decreases over this limit. At 334 nm (Jones and Wayne [9]), the photodissociation of ozone leads to O(³P) atoms only. In our models, two extreme values have been used in order to make a sensitivity evaluation. We prefer the maximum value since new measurements by Simonaitis *et al* [10] indicate a quantum efficiency of about 0.5 at 313 nm.

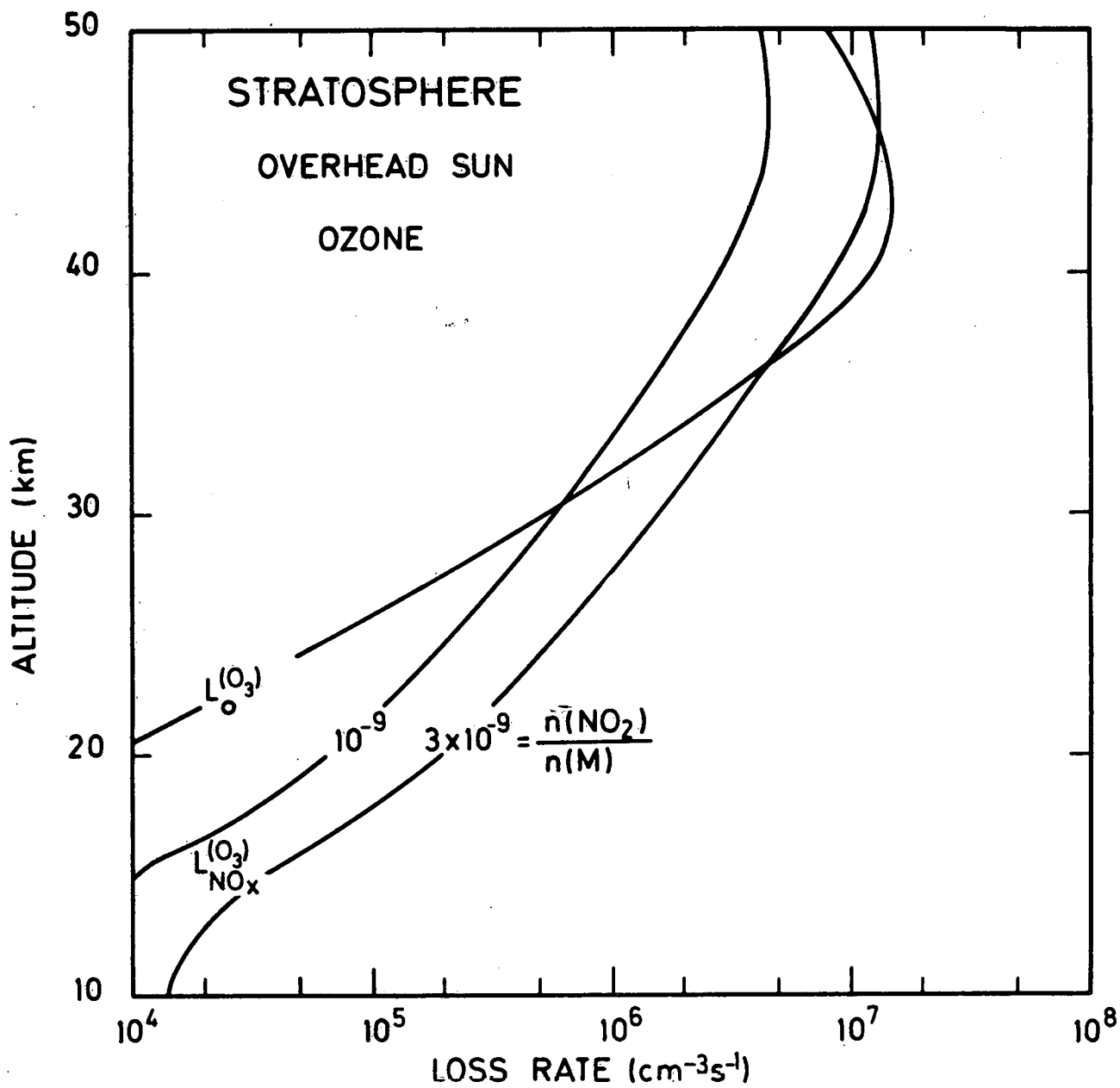
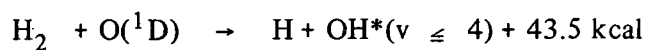
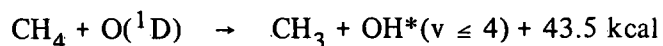
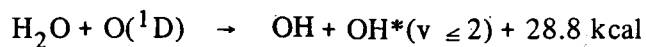


Fig. 2.- Loss rate of ozone by the Chapman reactions (L_{O_3}) and by the NO_x reactions (L_{NO_x}) for mid-latitude conditions and an overhead sun. L_{NO_x} has been computed using the constant values of 1 and 3 ppbv as NO_2 mixing ratio.

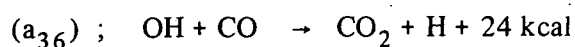
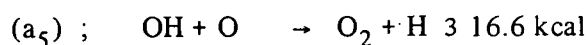
The O(¹D) atoms are quickly destroyed by quenching with O₂ and N₂ but a fraction of them dissociate water vapor, methane and molecular hydrogen to produce OH and H radicals



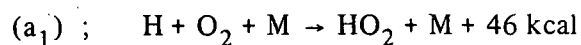
In the stratosphere, the water vapor mixing ratio remains constant and is of the order of 3 ppmv. Methane is produced at ground level, diffuses upward and is dissociated by OH or O(¹D). Its mixing ratio at the tropopause is of the order of 1.5 ppmv. The corresponding value for molecular hydrogen is 0.5 ppmv.

Other reactions involving OH, H and HO₂ must be introduced in order to determine the equilibrium conditions between these radicals (fig. 3) :

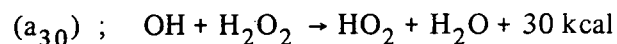
- H formation and OH destruction :



- HO₂ formation and H destruction



- HO₂ formation and OH destruction



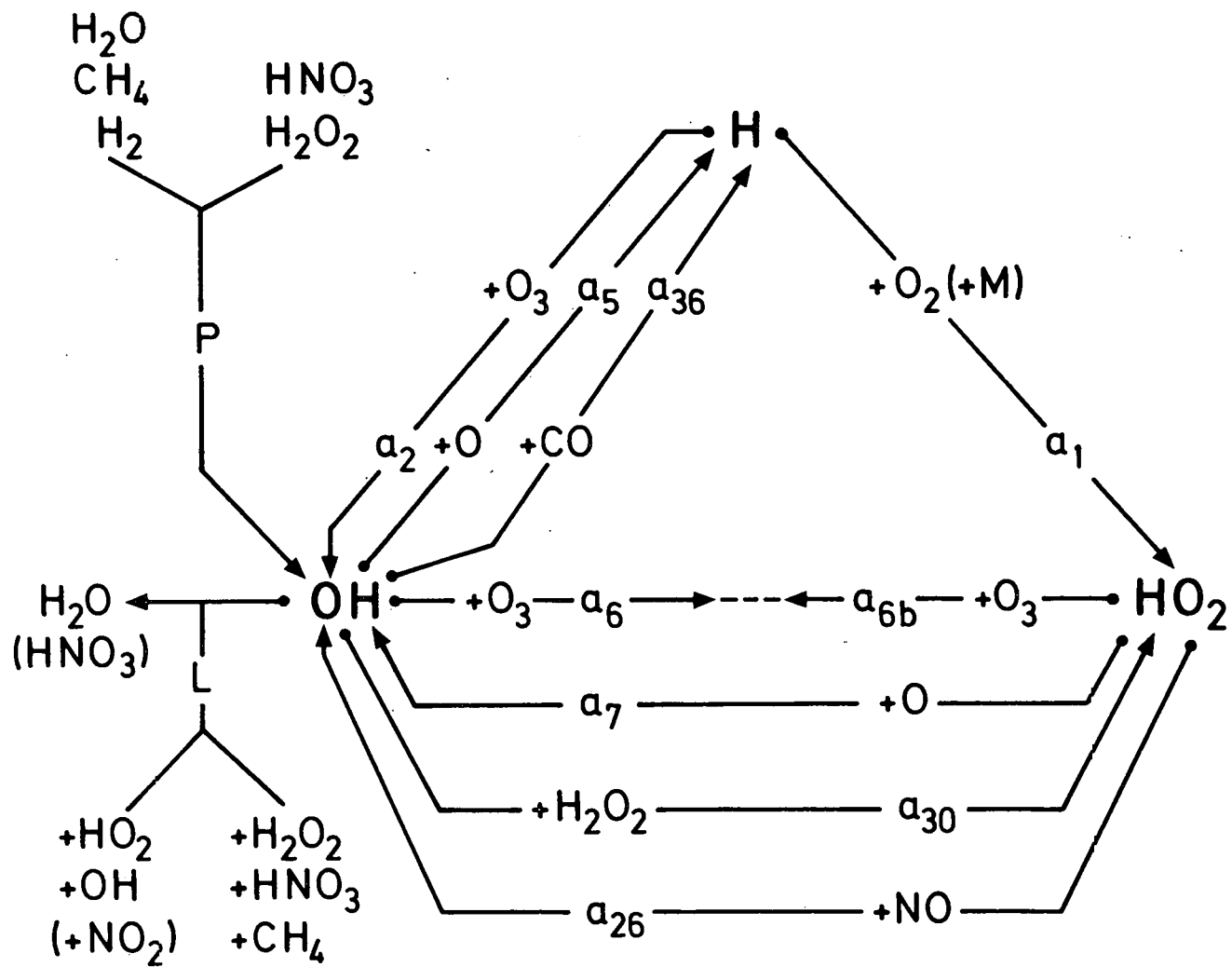
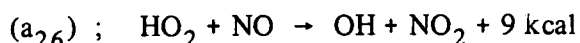
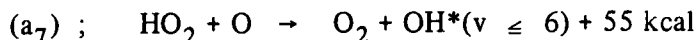


Fig. 3.- Reaction scheme showing the OH - H - HO₂ cycle in the stratosphere.

- OH formation and HO₂ destruction



These different mechanisms have been studied with great attention by several authors (see e.g. Nicolet [2]) and won't be discussed in detail here. However, it can easily be seen that the ratio $n(\text{HO}_2)/n(\text{OH})$ is

$$\frac{n(\text{HO}_2)}{n(\text{OH})} = \frac{a_5 n(\text{O}) + a_{36} n(\text{CO})}{a_7 n(\text{O}) + a_{26} n(\text{NO})} \left[\frac{a_1 n(\text{M}) n(\text{O}_2)}{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)} + \frac{a_{30} n(\text{H}_2\text{O}_2)}{a_5 n(\text{O}) + a_{36} n(\text{CO})} \right]$$

In the upper stratosphere, it simply becomes

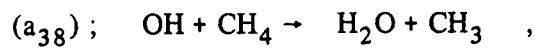
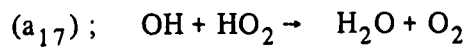
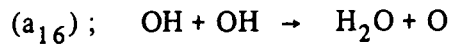
$$\frac{n(\text{HO}_2)}{n(\text{OH})} = \frac{a_5}{a_7} \times \frac{a_1 n(\text{M}) n(\text{O}_2)}{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)} \approx \frac{a_5}{a_7}$$

and near the tropopause

$$\frac{n(\text{HO}_2)}{n(\text{OH})} = \frac{a_{36} n(\text{CO}) + a_{30} n(\text{H}_2\text{O}_2)}{a_{26} n(\text{NO})}$$

This ratio, which plays a major role in the stratospheric photochemistry and specially (see below) on nitrogen oxides and acids cannot be evaluated since the rate constants a_5 and a_7 and the concentrations of carbon monoxide, nitric oxide and hydrogen peroxide are not known with enough precision. However working values have been used, namely 1 and 9 for the $n(\text{HO}_2)/n(\text{OH})$ ratio.

If we finally introduce the net loss mechanisms of HO_x reforming water vapor



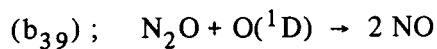
the global balance equation for NO_x can be written

$$a^*[n(\text{H}_2\text{O}) + n(\text{CH}_4) + n(\text{H}_2)] = a_{16} n^2(\text{OH}) + a_{17} n(\text{OH}) n(\text{HO}_2) + a_{38} n(\text{CH}_4) n(\text{OH}) .$$

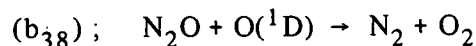
In a more detailed study, nitric acid should also be introduced in the HO_x problem since, as it will be seen below, it contributes to the OH formation and destruction. Nevertheless, it can be seen that the OH concentration closely depends on the nitrogen and the carbon oxides chemistry which must be studied with much attention. (see for example Brasseur and Nicolet [11] and Nicolet and Peetermans [12]).

4. THE NO_x PHOTOCHEMISTRY IN THE STRATOSPHERE

It was believed until a few years ago that the presence of nitrogen oxides in the stratosphere was due to its production above 90 km and its downward transport by eddy diffusion. However, in 1970, Nicolet [2] has identified an *in situ* source of NO due to the dissociation of nitrous oxide by ^1D oxygen atom



associated with



The stratospheric production of NO is thus given by

$$P(\text{NO}) = 2 b_{39} n(\text{N}_2\text{O}) n(\text{O}^1\text{D})$$

Nitrous oxide is formed by bacteria at ground level and diffuses into the stratosphere. But, during daytime, it is photodissociated by solar radiation and about ten per cent of it is destroyed by reactions (b₃₈) and (b₃₉). The N₂O distribution is thus very sensitive to the transport conditions ; the eddy flux Φ is related to the concentration n by

$$\Phi = -K \left[\frac{\partial n}{\partial z} + \frac{n}{H} + \frac{n}{T} \frac{\partial T}{\partial z} \right]$$

where H is the atmospheric scale height and T the temperature. In the troposphere, where the mean residence time is 1 month, the adopted value for the eddy diffusion coefficient K is $2 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$. But in the stratosphere, where the mean residence time varies between 1 to 2 years, a value between 10^3 and $10^4 \text{ cm}^2 \text{ s}^{-1}$ must be adopted. Since there are variations with season and latitude, two analytical profiles (K_{min} and K_{max}) which seem to represent acceptable values have been chosen (fig. 4) in order to estimate the sensitivity of the profiles to the transport intensity.

The vertical distribution of the NO production (fig.5) depends not only on the eddy diffusivity profile but also on the ozone distribution and the efficiency of its photodissociation to form O(¹D) atoms. The NO production rate reaches a maximum value of the order of $100 \text{ cm}^3 \text{ s}^{-1}$ in the middle of the stratosphere. The values represented on fig. 5 have been divided by 2 in order to take into account the day and night effect.

The total NO production by reaction O(¹D) with N₂O is about $(1.5 \pm 1) \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ (Nicolet and Peetermans [13]), which is the same order of magnitude as the artificial production by a conventional fleet of 500 SST aircrafts (334 equipped with 4 engines and 166 with 2 engines), flying 7 hours a day and emitting 10 ± 2.5 grams of NO per kilogram of fuel consumed.

As soon as it is produced a fraction of the NO molecules is converted into NO₂ molecules by reaction (b₄) which is associated with (b₃) and (J_{NO_2}) (fig. 6). Since the lifetime of NO₂ is very short during daytime, photochemical conditions can be accepted and the NO₂/NO ratio is given by (fig. 7)

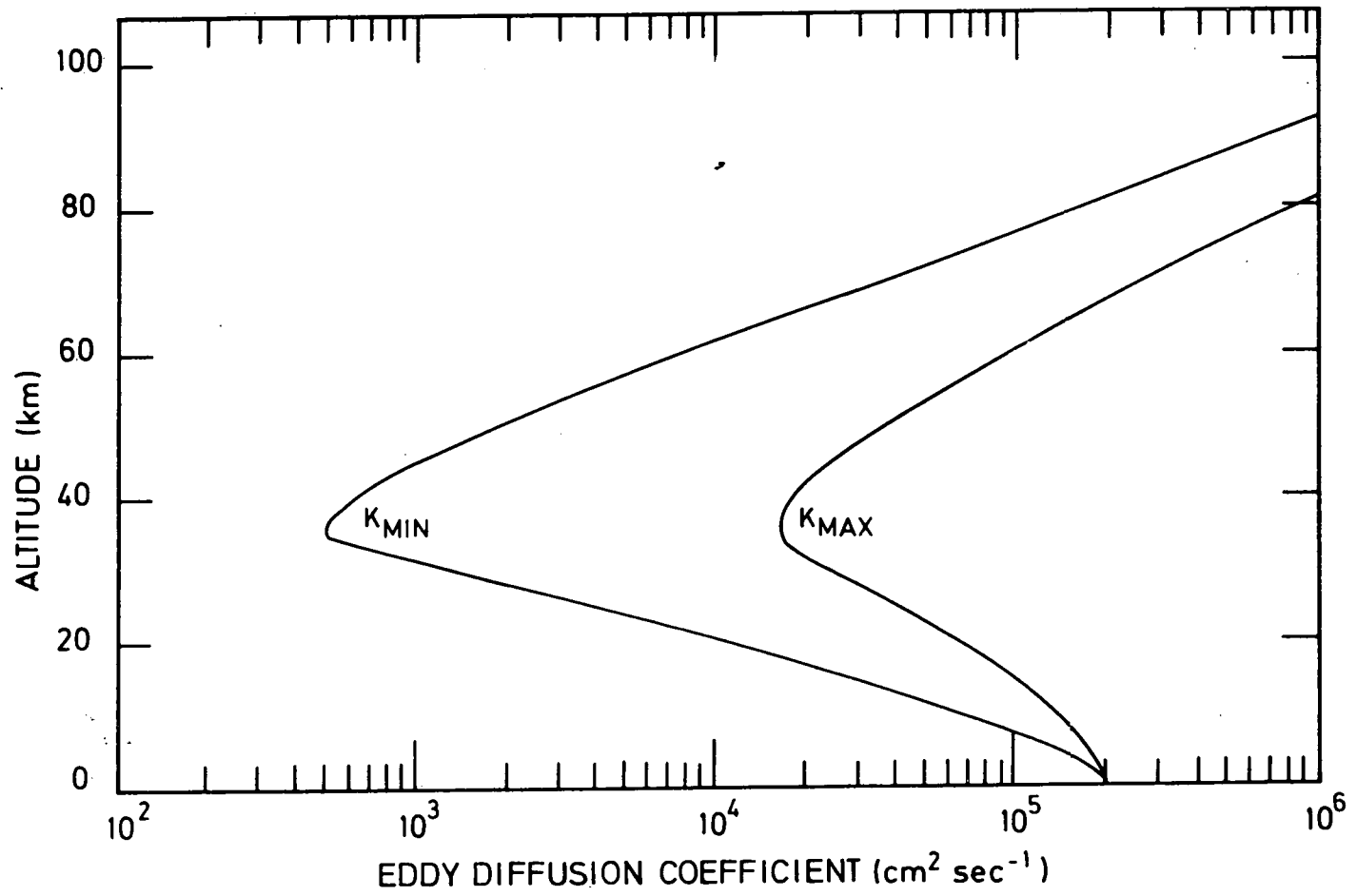


Fig. 4.- Variable values of the eddy diffusion coefficient with altitude used in the computations.

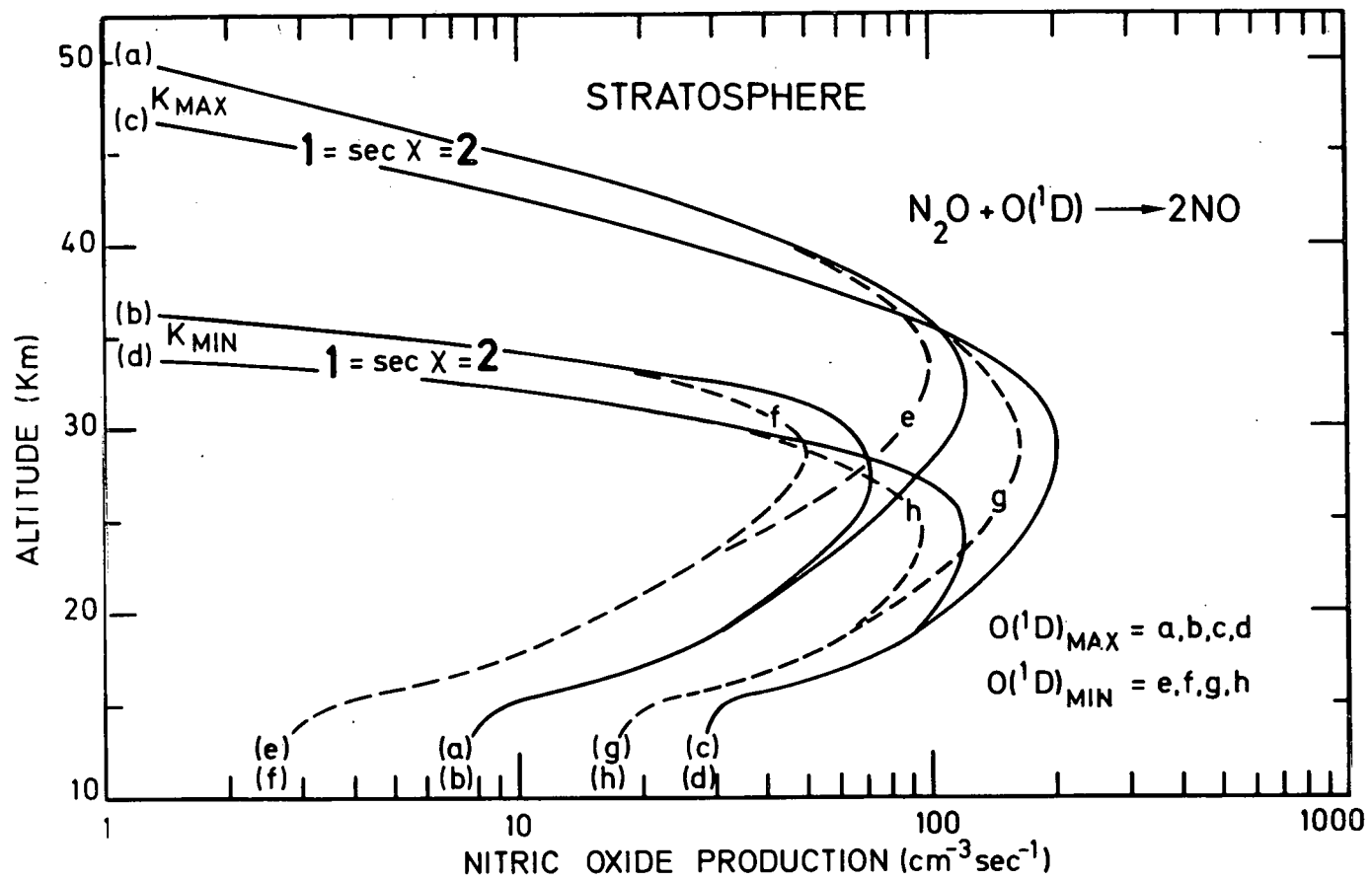


Fig. 5.- Vertical distribution of NO production for various stratospheric conditions.

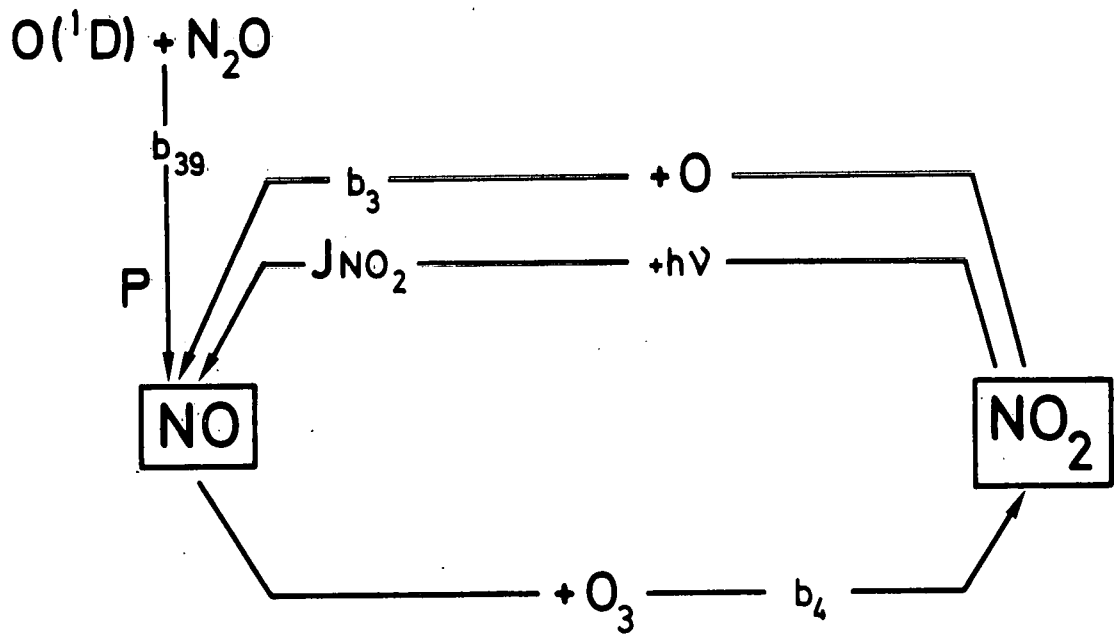


Fig. 6.- NO - NO₂ cycle.

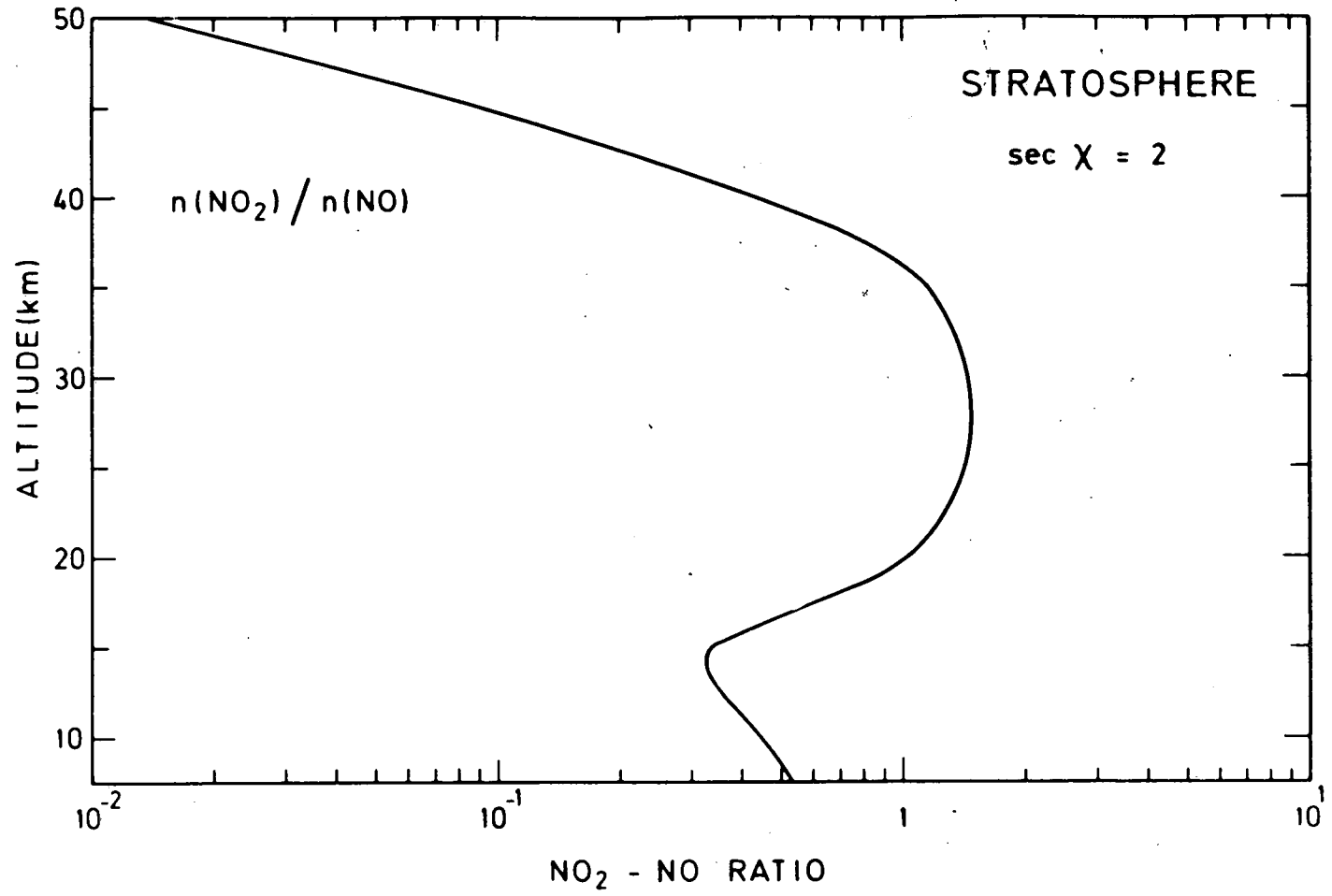
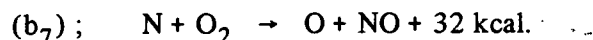
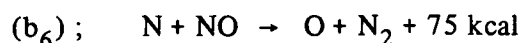
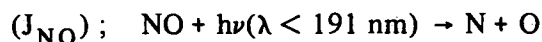


Fig. 7.- Vertical distribution in the stratosphere of the ratio $n(\text{NO}_2)/n(\text{NO})$ for a solar zenith angle of 50° .

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

In the lower part of the stratosphere where the oxygen atom concentration is small, the ratio is proportional to the ozone concentration and its order of magnitude is one. Above 35 km, where $J_{\text{NO}_2} \ll b_3 n(\text{O})$, the ratio decreases rapidly to reach less than 0.05 at 50 km. During nighttime, NO is completely converted into NO₂.

In the upper part of the stratosphere and above the stratopause, the photodissociation of NO must be considered as an important loss process for NO_x (Brasseur and Cieslik [14]) since we have (fig. 8)



The most important contribution to the photodissociation coefficient J_{NO} is due to the predissociation in the δ bands, mainly the $\delta(0-0)$ and $\delta(1-0)$ bands since the ϵ band have been shown by Callear and Pilling [15] not to be predissociated and since the β and γ bands have very small absorption coefficients. In the spectral range that must be consider, the absorption of the solar radiation is due in part to the Schumann-Runge bands of molecular oxygen. So, a line by line integration is necessary in order to compute the J_{NO} coefficient (fig. 9). A detailed analysis of this question has been performed by Cieslik and Nicolet [16] who have shown that it is not possible to deduce equivalent average cross sections which are not altitude dependant.

The net loss rate of nitrogen oxides $L(\text{NO})$ is given by

$$L(\text{NO}) = \frac{2 b_6 J_{\text{NO}} n^2(\text{NO})}{[b_7 n(\text{O}_2) + b_6 n(\text{NO})]}$$

$N_2 + hv$, etc...

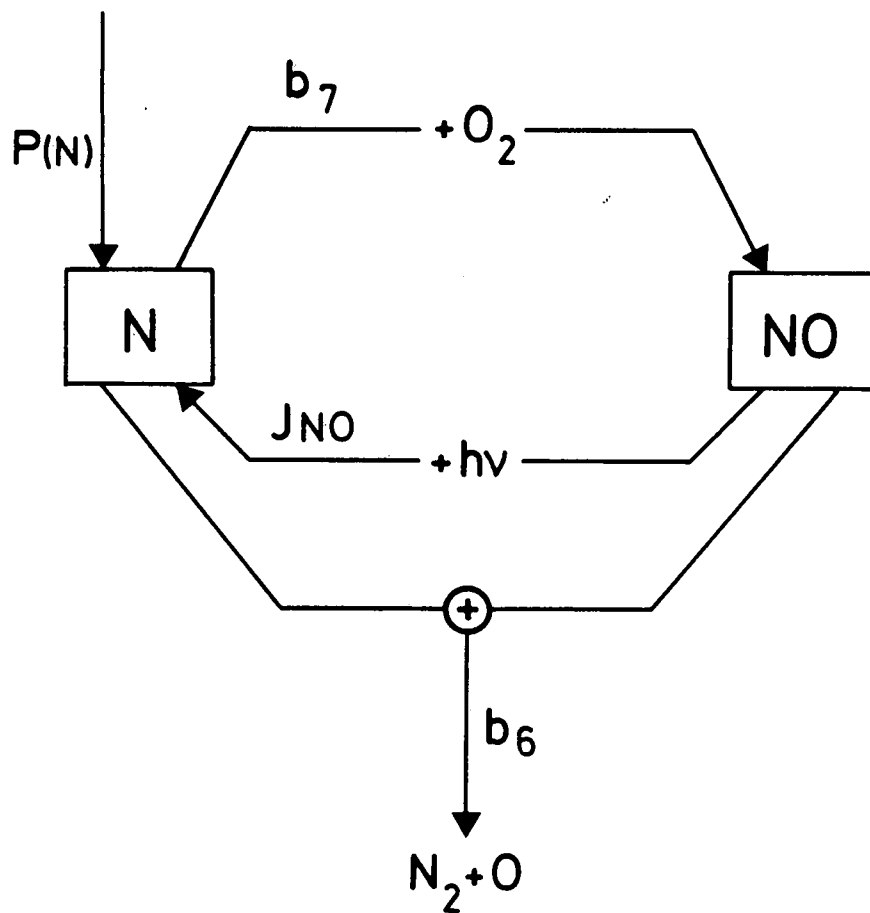


Fig. 8.- Important reactions involving N and NO in the mesosphere and stratosphere.

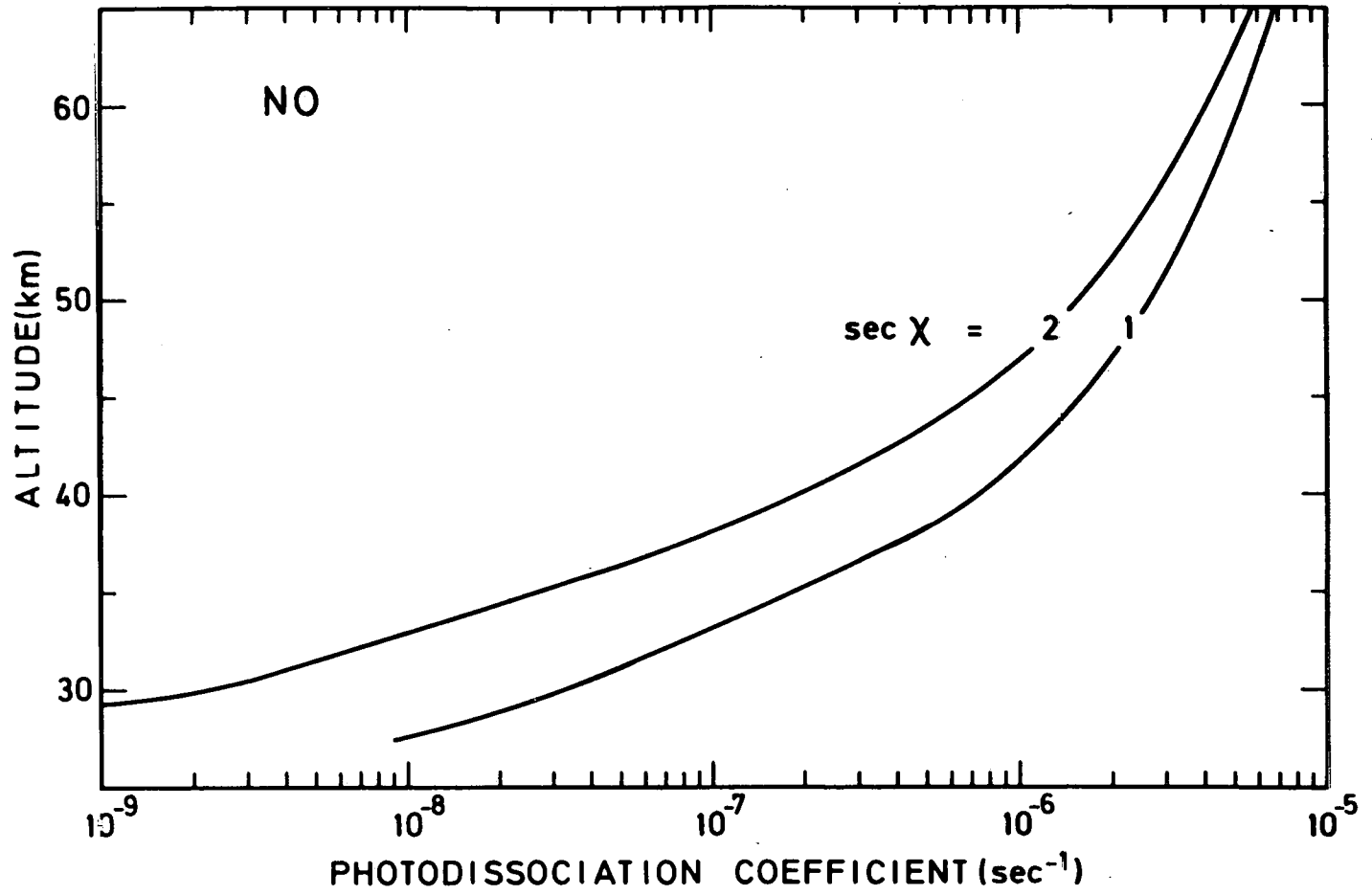


Fig. 9.- Photodissociation coefficient of NO versus altitude for an overhead sun and a zenith angle of 60°.

and is represented on fig. 10 where it is compared with the production and transport rate.

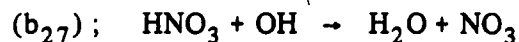
In the middle and lower stratosphere, other chemical reactions involving odd nitrogen atoms in polyatomic molecules must be introduced. The most important constituent certainly is nitric acid on which we shall confine our attention (fig. 11).

This constituent is mainly produced by the reaction

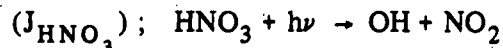


which can be considered as a three body reaction above 20 km and a two body reaction at sufficient high pressure.

Nitric acid is destroyed by hydroxyl radicals



and is photodissociated by ultraviolet light



with a quantum yield which seems to be equal to unity in the 190-300 nm spectral range (Johnston, private communication). Those reactions cannot be considered as net loss processes for odd nitrogen since there is a reformation of nitrogen di- and trioxides.

The absorption cross sections of HNO_3 has been measured by Dalmon [17], Johnston and Graham [18] and Biaumé [19]. From these data, the photodissociation coefficient at zero optical depth is found to be $1.7 \times 10^{-4} \text{ s}^{-1}$ for $\lambda = 185 - 345 \text{ nm}$. Its variation with altitude is represented on fig. 12.

Considering photochemical equilibrium conditions the ratio between the HNO_3 and NO_2 concentration is given by

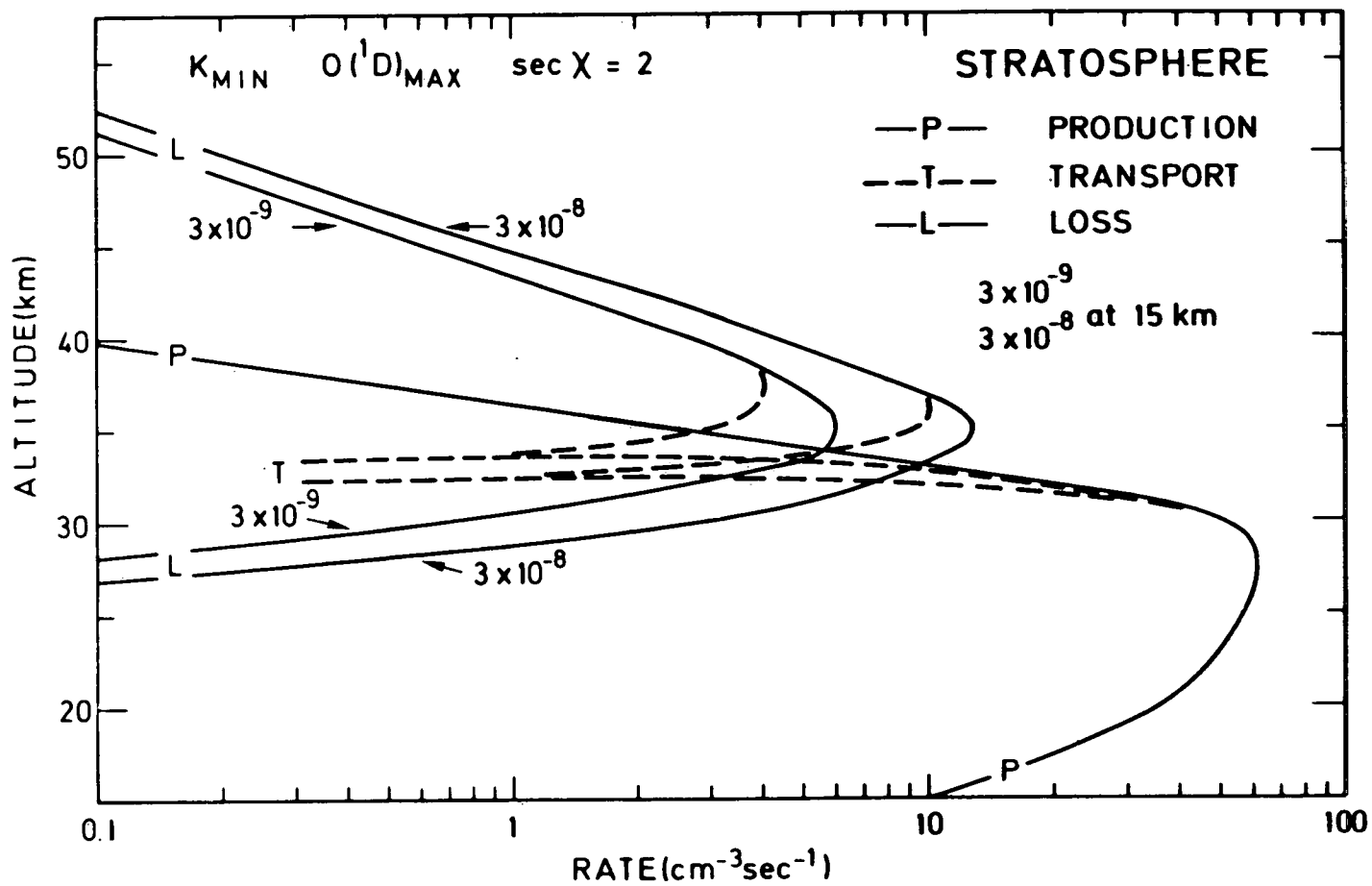


Fig. 10.- Production, transport and loss rates which can be considered as the most probable in the stratosphere. The production term may increase in the lower part of the stratosphere by the cosmic ray effect.

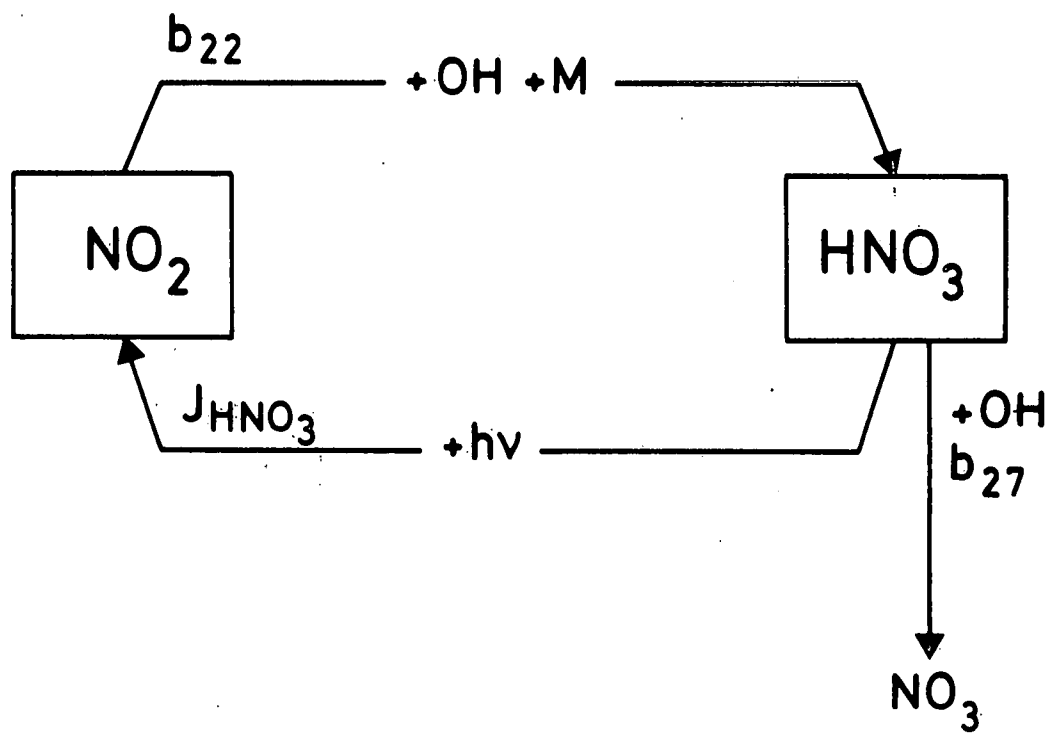


Fig. 11.- Reaction scheme showing the formation and destruction of nitric acid.

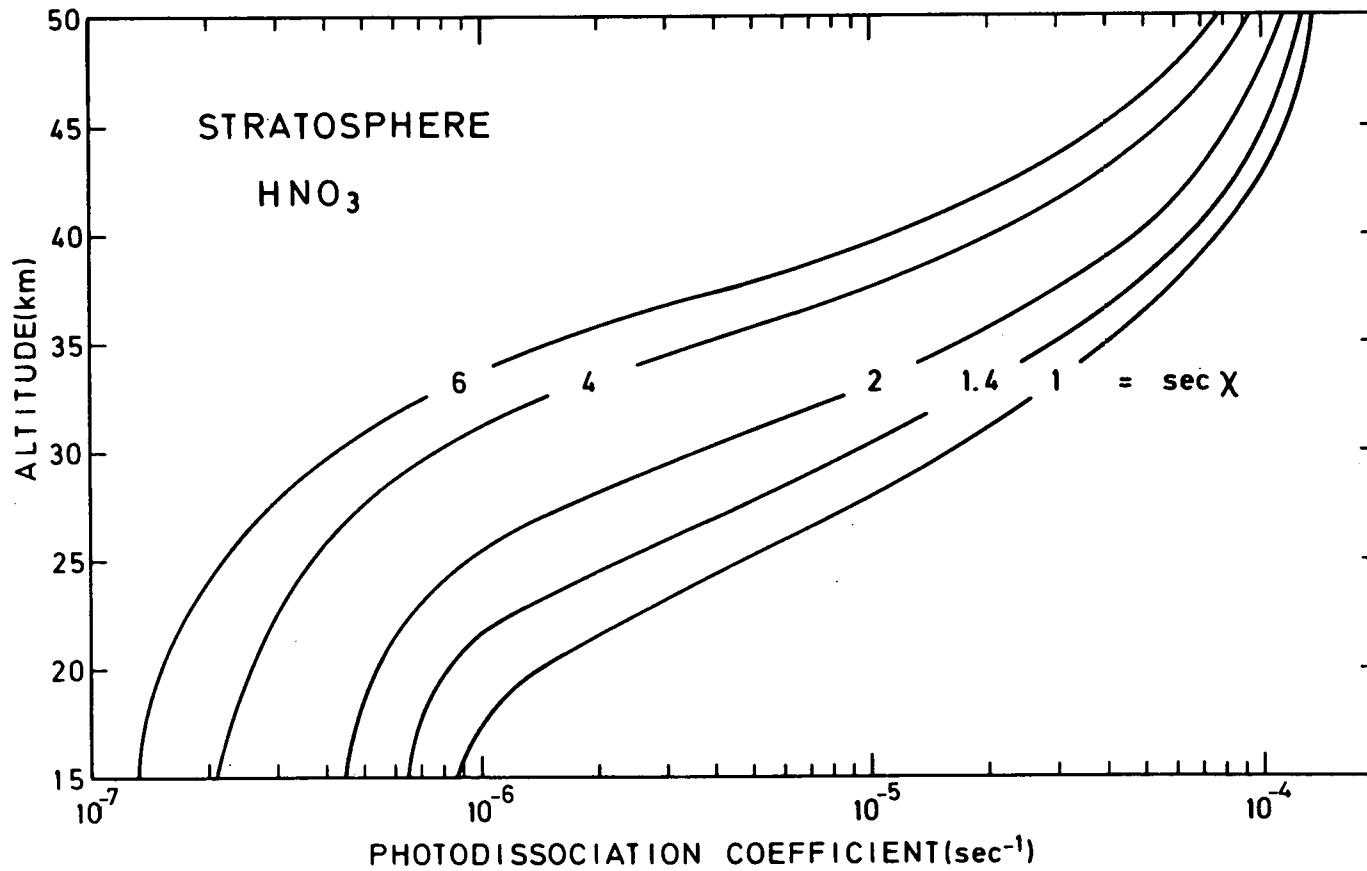
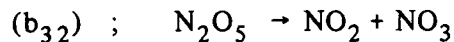
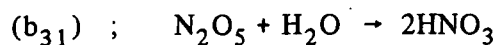
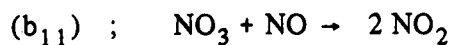
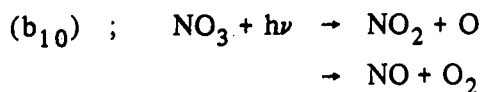
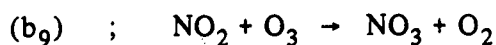


Fig. 12.- Photodissociation coefficient of nitric acid versus altitude for different values of the solar zenith angle and assuming a quantum efficiency equal to one.

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

and is represented on fig. 13. During daytime, the ratio is larger than 1 in the lower stratosphere but it decreases rapidly above 35 km. It must be pointed out that the hydroxyl concentration plays an important role since HNO_3 and thus NO_2 and NO are very sensitive to OH . The hydrogen-oxygen atmosphere must thus be studied carefully since an introduction of water vapor or methane in the lower stratosphere reduces the concentration of nitrogen oxides. An example of calculated NO , NO_2 and HNO_3 distributions is shown on fig. 14.

In order to treat the general problem of nitrogen oxides, NO_3 and N_2O_5 must also be introduced. Their principal reactions are (see Brasseur and Nicolet [11])



Photochemical assumptions give

$$n(\text{NO}_3) = \frac{b_9 n(\text{O}_3) n(\text{NO}_2) + b_{32} n(\text{N}_2\text{O}_5) + b_{27} n(\text{OH}) n(\text{HNO}_3)}{b_{10} + b_{11} n(\text{NO}) + b_{12} n(\text{NO}_2)}$$

and

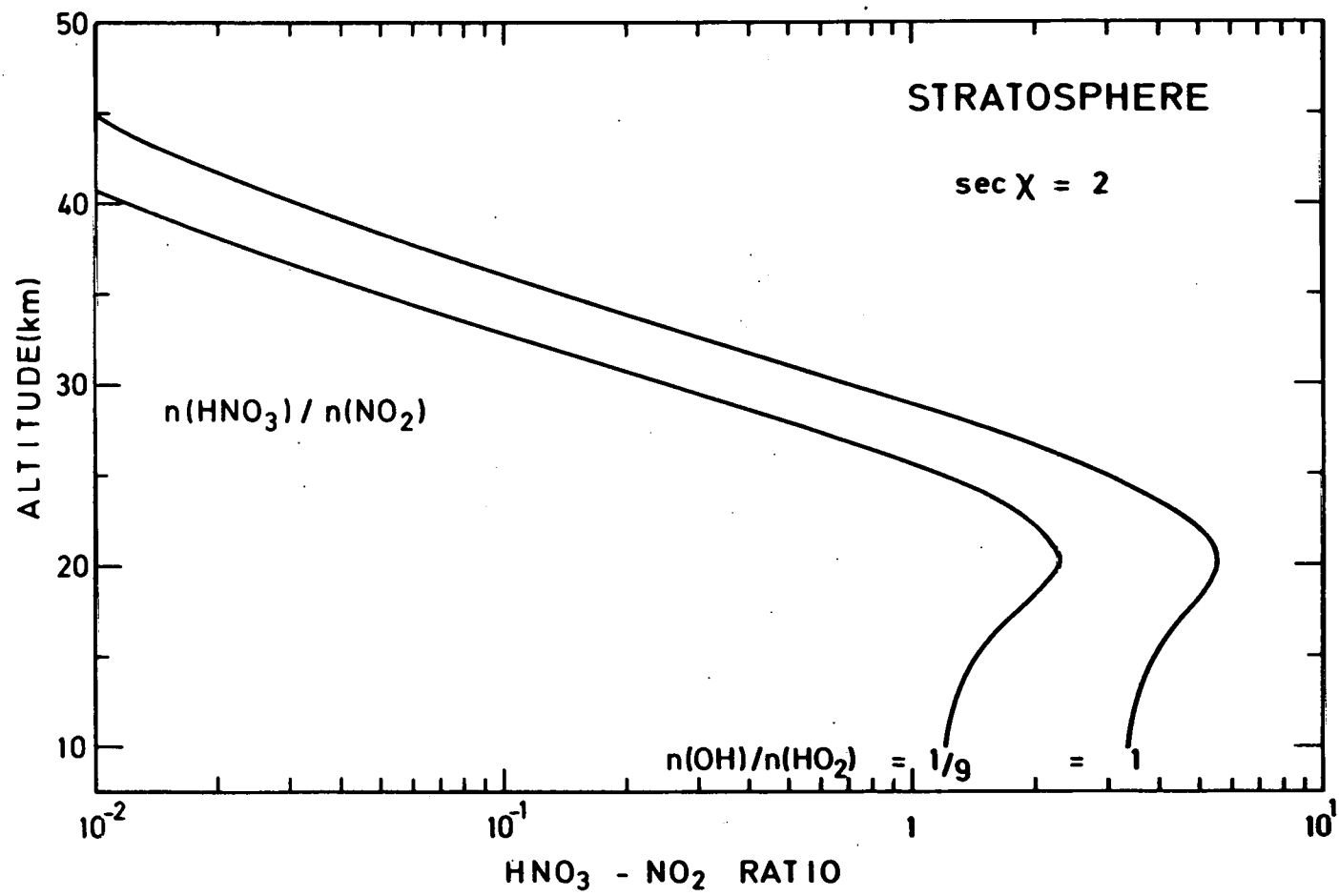


Fig. 13.- Vertical distribution in the stratosphere of the ratio $n(\text{HNO}_3)/n(\text{NO}_2)$ for a solar zenith angle of 60° and assuming two different ratios $n(\text{OH})/n(\text{HO}_2)$.

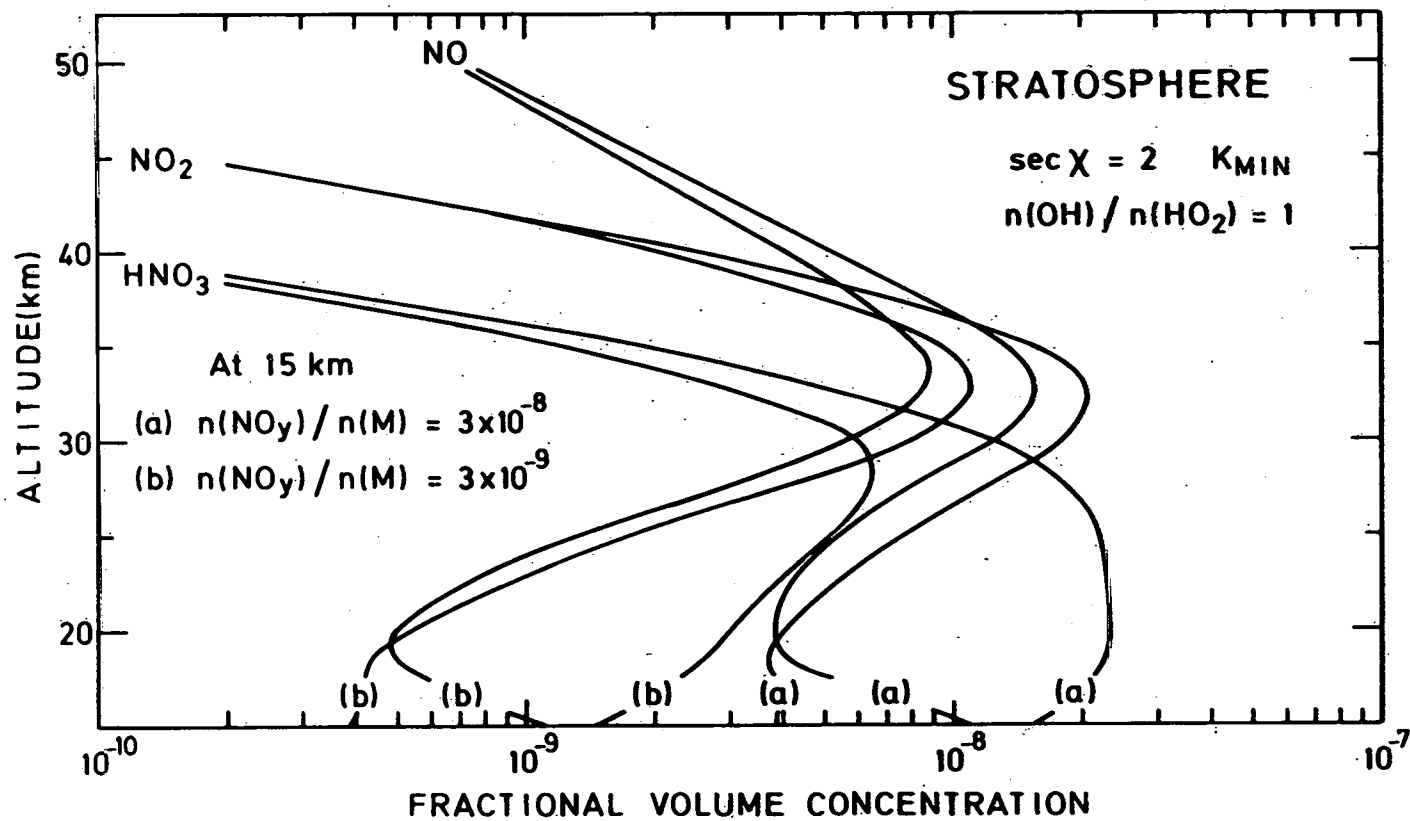


Fig. 14.- Vertical distribution of NO, NO₂ and HNO₃ calculated for two different values of the lower boundary condition of NO_y = NO + NO₂ + HNO₃ and assuming a solar zenith angle of 60°, n(OH) = n(HO₂) and K = K_{min}.

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

5. CONCLUSION

The effect of nitrogen oxides on ozone cannot be neglected in the lower stratosphere. In general, the NO_x chemistry can be explained considering only the oxygen atmosphere. However, hydrogen compounds play an important role in the formation of nitric acid by OH and therefore there is a need to introduce all aeronomic reactions dealing with the formation and destruction of hydroxyl and hydroperoxyl radicals. Since the ratio between the OH and HO_2 distribution is sensitive to the nitrogen and carbon oxides chemistry, a general aeronomic model of the stratosphere must be built.

New values of the important rate constants and cross sections with quantum yields are needed as well as new observational data such as the recent measurements of NO_2 by Ackerman and Muller [20] of HNO_3 by Murcray *et al* [21] of NO_2 and HNO_3 by Harries [22] of CO by Seiler and Warneck [23] and of CH_4 by Ehhalt and Heidt [24].

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