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Chemospheric processes of nitric oxide
in the mesosphere and stratosphere

by

G. BRASSEUR and M. NICOLET

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FOREWORD

"Chemospheric processes of nitric oxide in the mesosphere and stratosphere" will be published in Planetary and Space Science.

AVANT-PROPOS

"Chemospheric processes of nitric oxide in the mesosphere and stratosphere" sera publié dans Planetary and Space Science.

VOORWOORD

"Chemospheric processes of nitric oxide in the mesosphere and stratosphere" zal verschijnen in "Planetary and Space Science."

VORWORT

"Chemospheric processes of nitric oxide in the mesosphere and stratosphere" wird in "Planetary and Space Science" veröffentlicht werden.

CHEMOSPHERIC PROCESSES OF NITRIC OXIDE IN THE MESOSPHERE AND STRATOSPHERE

by

G. BRASSEUR and M. NICOLET

Abstract

The behavior of nitrogen oxides in the stratosphere and mesosphere is discussed with the aid of a model which introduces the photodissociation of nitric oxide and the formation of nitric acid. The profiles of the nitric oxide, nitrogen dioxide and nitric acid concentrations are sensitive to the values of the eddy diffusion coefficients which are adopted. The evaluation of the various reactions which enter the stratosphere shows the role of the formation of nitric acid which is related to the production of OH radicals in the lower stratosphere. An increase of the water vapor in the stratosphere leads to a decrease of nitric oxide and nitrogen dioxide.

Résumé

La distribution des oxydes d'azote dans la stratosphère et la mésosphère est discutée dans un modèle où intervient la photodissociation du monoxyde d'azote et la formation de l'acide nitrique. Les profils de NO, NO₂ et HNO₃ dépendent de la valeur du coefficient de diffusion turbulente. L'évaluation des différentes réactions stratosphériques montre l'importance de la présence de l'acide nitrique qui dépend de la production des radicaux hydroxyls dans la stratosphère inférieure. Une augmentation de la vapeur d'eau dans la stratosphère conduit à une diminution du monoxyde et du dioxyde d'azote.

Samenvatting

De verdeling van stikstofoxyden in de stratosfeer en de mesosfeer wordt bestudeerd in een model waarbij NO gefotodissociëerd en salpeterzuur gevormd wordt. De profielen van NO, NO₂ en HNO₃ hangen af van de waarde van de turbulente-diffusiecoëfficiënt. De beschouwing der verschillende stratosferische reacties toont het belang van de tegenwoordigheid van salpeterzuur dat afhangt van de vorming van hydroxylradicalen in de benedenstratosfeer. Een toename van waterdamp in de stratosfeer leidt tot een vermindering van NO en NO₂.

Zusammenfassung

Die Verteilung der Stickstoffoxyde in der Stratosphäre und in der Mesosphäre wird in einem Model wo die Photodissoziation des Stickstoffmonoxydes und die Bildung der Salpetersäure vorkommen, behandelt. Die Profile des NO, NO₂ und des HNO₃ hängen von dem Wert des Wirbelnden Diffusionskoeffizienten ab. Die Abschätzung der verschiedenen stratosphärischen Reaktionen zeigt die Bedeutung der Salpetersäure, das von der Produktion der OH Radikalen in der unteren Stratosphäre abhängt. Eine Steigerung des Wasserdampfes in der Stratosphäre leitet zu einer Rücknahme des Stickstoffmonoxyds und -dioxys.

I. INTRODUCTION

The theory of nitric oxide in the earth's atmosphere must be based on the ionospheric properties in the F and E regions (Norton and Barth, 1970; Strobel *et al*, 1970; Nicolet, 1970a; Strobel 1971a, 1971b). Ionic reactions lead to excited atoms $N(^2D)$ which react with O_2 in order to form nitric oxide molecules. In addition, dissociative ionization in the E and D regions is also a source of odd nitrogen atoms since solar X rays of $\lambda < 31\text{\AA}$ lead to mostly dissociative ionization (Van Brunt *et al*, 1972). As far as cosmic rays are concerned, it is clear (Nicolet and Aikin, 1961; Nicolet and Peetermans, 1972) that an important fraction of the ionization leads to dissociative ionization of molecular nitrogen and, therefore, to a production of nitric oxide through the reaction of nitrogen atoms in the normal state with molecular oxygen.

The aeronomic behavior of NO in the D region requires, however, a different analysis (Strobel, 1972) since it strongly depends on its dissociation rate.

The photodissociation coefficient of nitric oxide in the mesosphere and stratosphere is difficult to calculate since the atmospheric attenuation depends on the absorption by the Schumann-Runge bands of O_2 . Such a calculation has recently been made by Cieslik and Nicolet (1973) by using detailed-cross sections values of molecular oxygen determined by Ackerman *et al* (1970) and Kockarts (1972). The total photodissociation coefficient of NO which is adopted here is of the order of 10^{-5} sec^{-1} at the mesopause level for a solar zenith angle of 60° , reaches about 10^{-6} sec^{-1} near the stratopause and is not far from 10^{-9} sec^{-1} at 30 km. With such values of the daytime dissociation coefficient of NO, an attempt is made to estimate the mesospheric and stratospheric abundances of nitric oxide. In addition various parameters are considered in order to determine the possible variations in the production of nitrogen oxides in the stratosphere and also the simultaneous vertical distribution of nitric oxide, nitrogen dioxide and nitric acid.

II. AERONOMIC REACTIONS IN THE CHEMOSPHERE

If we consider the various reactions which are involved in the mesosphere and stratosphere, it is clear that atomic nitrogen has a very short lifetime since reactions such as (see Nicolet 1965, 1970)



are normal aeronomic processes. In fact, below the mesopause, the principal process is reaction (3) which can be written in different ways from

$$b_7 = 5 \times 10^{-13} T^{1/2} e^{-3500/T} \text{ cm}^6 \text{ sec}^{-1} \quad (4a)$$

to
$$b_7 = 2.2 \times 10^{-13} T^{1/2} e^{-3100/T} \text{ cm}^6 \text{ sec}^{-1} \quad (4b)$$

or
$$b_7 = 7.5 \times 10^{-15} T e^{-3000/T} \text{ cm}^6 \text{ sec}^{-1} \quad (4c)$$

according to recent laboratory determinations; Becker *et al*, 1969 and ref. infra).

On the various aeronomic processes leading to the union of odd nitrogen atoms, only the following reaction (see Nicolet, 1965) is important



with a rate coefficient known within a factor of two

$$b_6 = (1.5 \pm 0.5) \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} , \quad (6)$$

which may represent the laboratory measurements (Philipps and Schiff, 1962 ; Schiff, 1969; Baulch *et al*, 1969).

If we now choose for aeronomic conditions the *chemical* equilibrium of nitric oxide, the equation is simply

$$n_*(\text{NO}) = b_7 n_7 / b_6 \quad (7)$$

where the n_7 indicates the particle concentration (here molecular oxygen). However, in addition to the nitric oxide loss process (5), account must be taken of the photodissociation. The predissociation, which was introduced by Bates (1952) as an aeronomic process



leads to

$$\frac{n(\text{NO})}{n(\text{N})} = \frac{b_7 n_7}{J_{\text{NO}} + b_6 n(\text{N})} \quad (9)$$

which corresponds to photochemical equilibrium conditions if J_{NO} is the photodissociation coefficient of NO.

In fact, considering an atomic nitrogen production, we must write

$$\frac{dn(\text{N})}{dt} + n(\text{N}) [b_6 n(\text{NO}) + b_7 n(\text{O}_2)] = n(\text{NO}) J_{\text{NO}} + P(\text{N}) \quad (10)$$

in which the last term on the right takes into account any possibility of atomic nitrogen production by direct or indirect dissociation of molecular nitrogen. In the mesosphere and stratosphere, the life-time of atomic nitrogen is very short and chemical equilibrium is reached very rapidly. It is, therefore, evident that the following equation can be used

$$n(\text{N}) = \frac{n(\text{NO}) J_{\text{NO}} + P(\text{N})}{b_6 n(\text{NO}) + b_7 n(\text{O}_2)} \quad (11)$$

The differential equation related to the variation of the nitric oxide concentration is

$$\frac{dn(\text{NO})}{dt} + n(\text{NO}) [J_{\text{NO}} + b_6 n(\text{N})] = b_7 n(\text{O}_2) n(\text{N}) + P(\text{NO}) \quad (12)$$

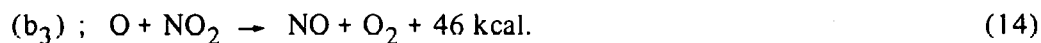
in which $P(\text{NO})$ is an independent source of NO, which has been identified by Nicolet (1970b) as coming from N_2O reacting with $\text{O}(^1\text{D})$ produced by the ozone photodissociation. Such a source has also been adopted by Crutzen (1971), McElroy and McConnell (1971), Nicolet and Vergison (1971), Nicolet and Peetermans (1972), Johnston (1972), etc.

Thus, the general photochemical conditions which can be applied to NO and N are, from (11) and (12),

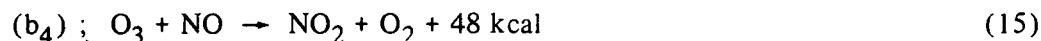
$$\frac{dn(N)}{dt} + \frac{dn(NO)}{dt} + 2b_6 n(NO) n(N) = P(N) + P(NO) \quad (13)$$

However, at stratospheric levels, in the ozonosphere, it is necessary to consider in the study of nitric oxide the reaction with ozone leading to NO₂ and subsequent reactions involving nitrogen trioxide, tetroxide and pentoxide (see Nicolet, 1965). Furthermore, since hydrogen compounds are present in the stratosphere, several important reactions of hydroxyl or hydroperoxyl radicals, which lead to nitrous and nitric acid, must be involved (Nicolet, 1965).

Two bimolecular processes in which NO and NO₂ are involved must be considered as important aeronomic reactions. The first one is a reaction with atomic oxygen



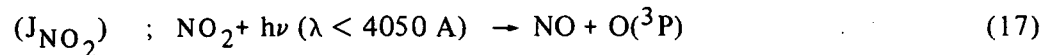
This is known to be rapid and the most recent measurements (Davis *et al*, 1972) indicate that the exact value should be $9 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$. The other reaction of nitric oxide with ozone leads to ground state NO₂ molecules



with a rate coefficient (Johnston and Crosby, 1954 ; Clough and Thrush, 1967), which can be given by

$$b_4 = (1 \pm 0.3) \times 10^{-12} e^{-1250/T} \text{ cm}^3 \text{ sec}^{-1} \quad (16)$$

In addition to these two reactions involving NO and NO₂, the photodissociation of NO₂ occurs in a sunlit atmosphere



with an average photodissociation coefficient at the stratopause

$$J_{\text{NO}_2} = 1 \times 10^{-2} \text{ sec}^{-1} \quad (18)$$

if the absorption cross sections of Hall and Blacett (1952) and relative yield of Jones and Bayes (1972) are adopted. The absorption in the stratosphere is very small and J_{NO_2} (15 km) is still of the order of $8 \times 10^{-3} \text{ sec}^{-1}$. Neglecting other possible reactions, we may write for stratospheric conditions

$$\frac{dn(\text{NO}_2)}{dt} + n(\text{NO}_2) [J_{\text{NO}_2} + b_3 n(\text{NO})] = b_4 n(\text{O}_3) n(\text{NO}) \quad (19)$$

and we must insert in (13) the reactions (14), (15) and (17) in order to consider all the processes involving NO_2 and NO . Nevertheless these reactions may be at once eliminated from the equations if we write

$$\frac{dn(\text{N})}{dt} + \frac{dn(\text{NO})}{dt} + \frac{dn(\text{NO}_2)}{dt} + 2b_6 n(\text{NO}) n(\text{N}) = P(\text{N}) + P(\text{NO}) \quad (20)$$

Furthermore, for daytime conditions, a photoequilibrium exists between NO and NO_2 and the ratio $n(\text{NO}_2)/n(\text{NO})$ is given by

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_4 n(\text{O}_3)}{J_{\text{NO}_2} + b_3 n(\text{O})} \quad (21)$$

An example of a vertical distribution of the ratio NO_2/NO in the stratosphere is given in Fig. 1. The ratio $n(\text{NO}_2)/n(\text{NO})$ is of the order of 1 in the major part of the stratosphere. However, it is less than 1 at 40km and decreases rapidly to become of the order of 10^{-2} at the stratopause. Finally, as conditions for explaining the lower stratosphere processes, we have other chemical reactions involving odd nitrogen atoms in polyatomic molecules such as the nitrous and nitric acids and other nitrogen oxides. They must be added to equation (20). Several of them may be at once eliminated since their action is not important. Among the various reactions (see Nicolet, 1965) we shall, therefore, confine here to the case of HNO_3 as principal constituent. In the most simple way, we consider the production of nitric acid by the reaction

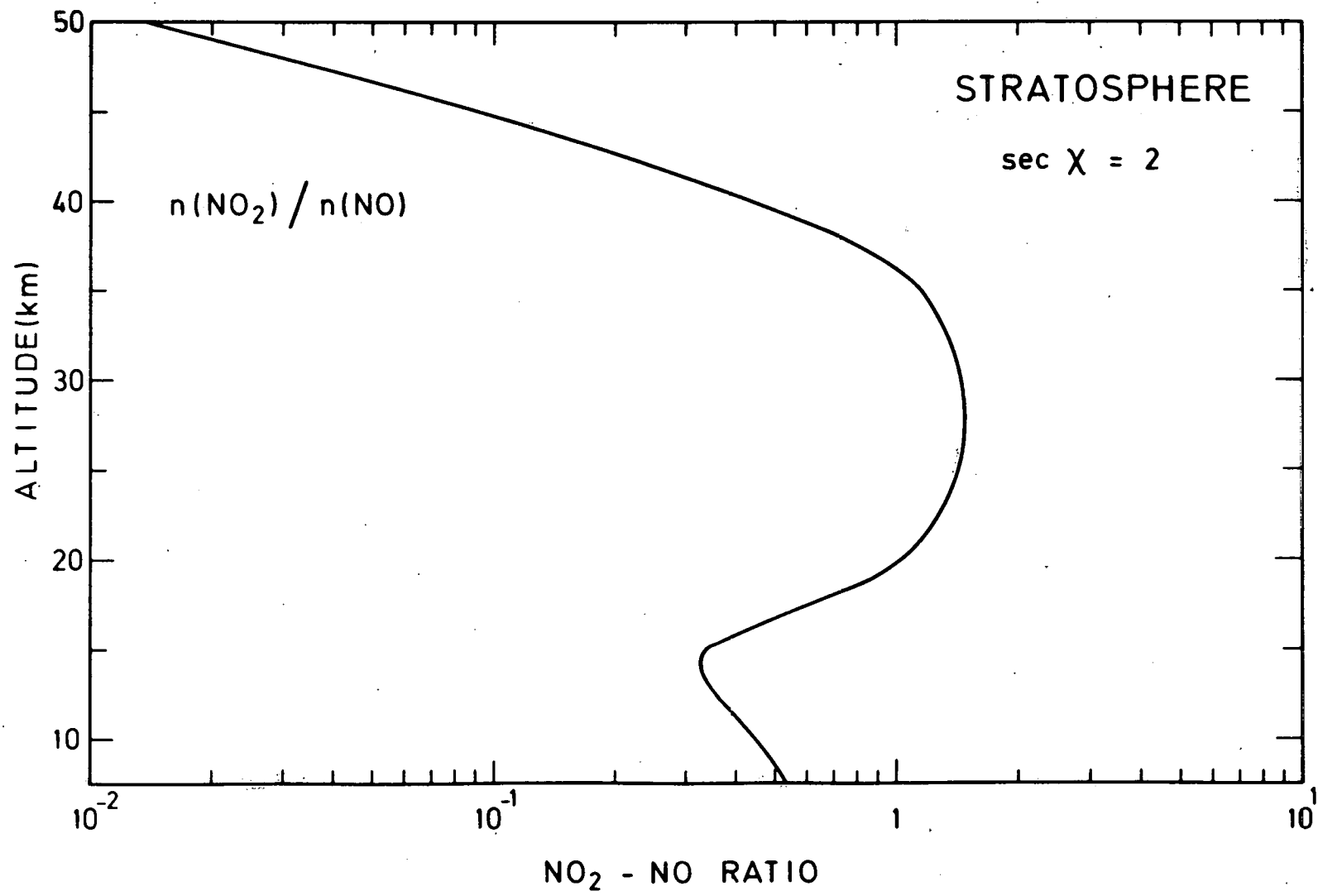
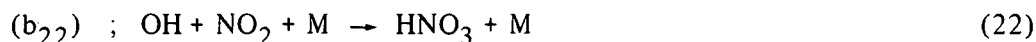


Fig. 1.- Vertical distribution in the stratosphere of the ratio $n(\text{NO}_2)/n(\text{NO})$ for a solar zenith angle of 60° .



which has been the subject of several laboratory measurements (Simonaitis and Heicklen, 1972; Morley and Smith, 1972; Anderson and Kaufman, (1972)). The rate coefficient of (22) is well determined and it can be taken as

$$b_{22} n(\text{He}) = (1.1 \pm 0.2) \times 10^{-30} n(\text{He}) \text{ cm}^3 \text{ sec}^{-1} \quad (23)$$

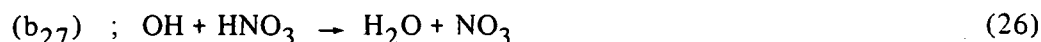
For an atmospheric constituent such as N_2 as third body (Anderson and Kaufman, 1972), the rate coefficient becomes

$$b_{22} n(\text{N}_2) = 2 \times 10^{-30} n(\text{N}_2) \text{ cm}^3 \text{ sec}^{-1} \quad (24)$$

which is a relatively high value. The high-pressure limiting rate coefficient seems to be of the order of

$$b_{22}^{\ell} = (5 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (25)$$

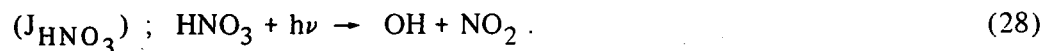
The principal bimolecular reaction in which HNO_3 is involved in the stratosphere should be



with a rate coefficient at 300°K (Hussain and Norrish, 1963.; Morley and Smith, 1972) of the order of

$$b_{27} = 1.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (27)$$

The possibility of finding a re-formation process for OH from HNO_3 is a photodissociation



HNO_3 absorption cross section measurements have been made by Biaumé (1972) in our laboratory. From his results we obtain the following photodissociation coefficient at zero optical depth

$$J_{\text{HNO}_3} = 3.5 \times 10^{-5} \text{ sec}^{-1} \quad (29)$$

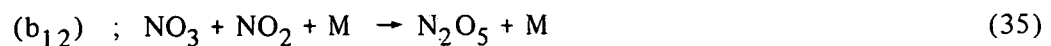
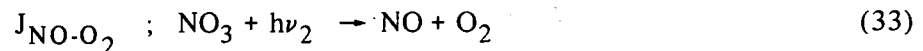
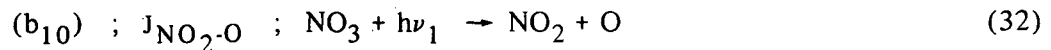
The variation with solar zenith angle at various altitudes in the stratosphere is illustrated by Fig. 2. The atmospheric model used by Nicolet (1970) has been adopted in order to determine the penetration of the solar radiation (Ackerman, 1971) in the chemosphere.

Neglecting the reaction between O and HNO₃, and keeping only the three last principal reactions, the photochemical equation of nitric acid thus becomes

$$\frac{dn(\text{HNO}_3)}{dt} + n(\text{HNO}_3) [J_{\text{HNO}_3} + b_{27} n(\text{OH})] = b_{22} n(\text{M}) n(\text{OH}) n(\text{NO}_2) \quad (30)$$

Examples of the ratio $n(\text{HNO}_3)/n(\text{NO}_2)$ are illustrated in Fig. 3 for photoequilibrium conditions and various values of $n(\text{OH})$ in the stratosphere. The ratio of nitric acid and nitrogen dioxide concentrations is greater than 1 in the lower stratosphere. The ratio decreases rapidly above 35 km (≤ 1) and reaches less than 1/10 in the upper stratosphere.

In order to treat the general problem, we must consider the effect of NO₃ and N₂O₅. The principal reactions for NO₃ are (see Nicolet, 1965 ; Johnston, 1970 ; Crutzen, 1971 ; Levy, 1972)



The photochemical equation has the form

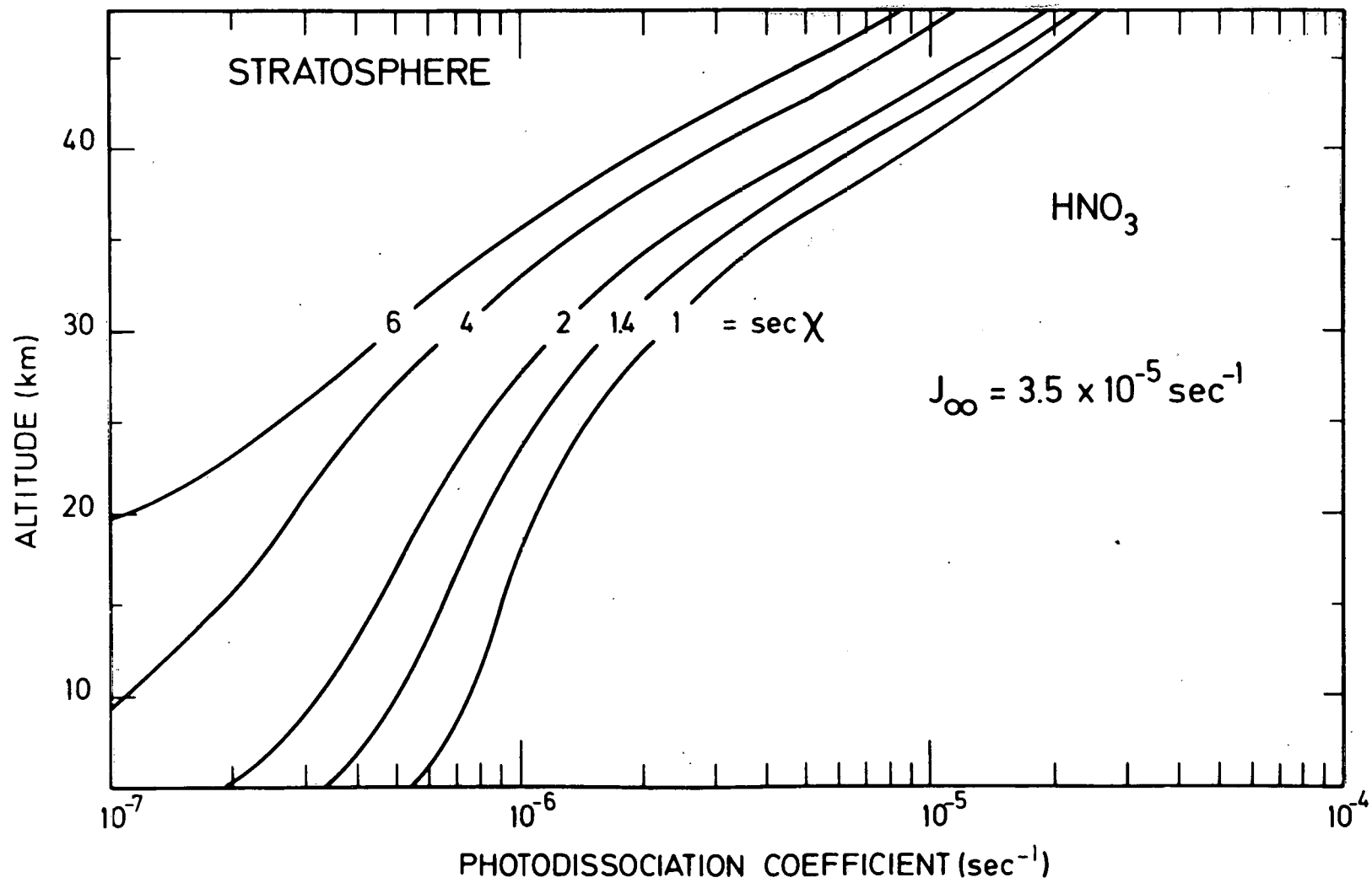
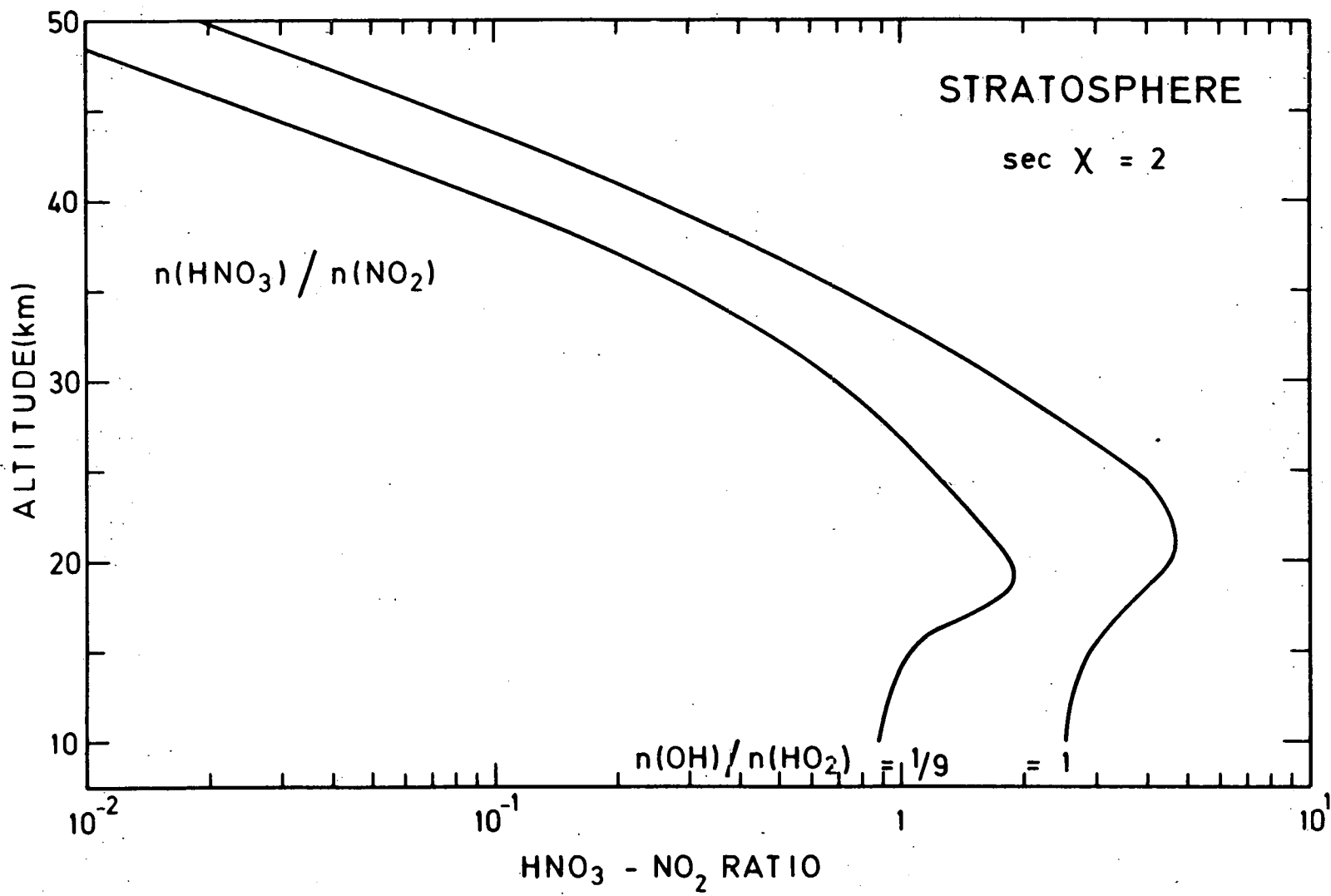


Fig. 2.- Photodissociation coefficient of nitric acid for various solar zenith angle ($\sec \chi = 1$, overhead sun, 1.4, 45° , 2, 60° , ...).



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Fig. 3.- Vertical distribution in the stratosphere of the ratio $n(\text{HNO}_3)/n(\text{NO}_2)$ for solar zenith angle of 60° and values of OH according to Nicolet and Peetermans (1973).

$$\begin{aligned} \frac{dn(\text{NO}_3)}{dt} + n(\text{NO}_3) [J_{\text{NO}_2\text{-O}} + J_{\text{NO-O}_2} + b_{11} n(\text{NO}) + b_{12} n(\text{NO}_2)] \\ = b_9 n(\text{O}_3) n(\text{NO}_2) + b_{32} n(\text{N}_2\text{O}_5) + b_{27} n(\text{OH}) n(\text{HNO}_3) \end{aligned} \quad (37)$$

Another reaction can be introduced for N_2O_5 ; it is



which leads to the photochemical equation

$$\frac{dn(\text{N}_2\text{O}_5)}{dt} + n(\text{N}_2\text{O}_5) [b_{32} + b_{31} n(\text{H}_2\text{O})] = b_{12} n(\text{M}) n(\text{NO}_2) n(\text{NO}_3) \quad (39)$$

By combining all equations without neglecting a term, we find that the differential photochemical equation for odd nitrogen atoms is

$$\begin{aligned} \frac{dn(\text{N})}{dt} + \frac{dn(\text{NO})}{dt} + \frac{dn(\text{NO}_2)}{dt} + \frac{dn(\text{NO}_3)}{dt} + 2 \frac{dn(\text{N}_2\text{O}_5)}{dt} + \frac{dn(\text{HNO}_3)}{dt} + \frac{dn(\text{HNO}_2)}{dt} \\ P(\text{N}) + P(\text{NO}) - 2b_6 n(\text{N}) n(\text{NO}) \end{aligned} \quad (40)$$

It will be convenient to write the left hand members above, $dn(\text{NO}_y)/dt$ which corresponds to

$$n(\text{NO}_y) = n(\text{N}) + n(\text{NO}) + n(\text{NO}_2) + n(\text{NO}_3) + 2 n(\text{N}_2\text{O}_5) + n(\text{HNO}_2) + n(\text{HNO}_3) \quad (41a)$$

and practically for the whole stratosphere

$$n(\text{NO}_y) = n(\text{NO}) + n(\text{NO}_2) + n(\text{HNO}_3) \equiv n(\text{NO}_x) + n(\text{HNO}_3) \quad (41b)$$

At the stratopause and in the mesosphere

$$n(\text{NO}_y) = n(\text{NO}) \quad ; \quad (41c)$$

in the upper stratosphere

$$n(\text{NO}_y) = n(\text{NO}) + n(\text{NO}_2) = n(\text{NO}_x) \quad (41d)$$

and in the lower stratosphere

$$n(\text{NO}_y) = n(\text{HNO}_3) + n(\text{NO}_2) + n(\text{NO}) \quad (41e)$$

III. THE CONTINUITY EQUATION

Introducing the equilibrium value (11) for the atomic nitrogen concentration into the general photochemical equation (40), the latter becomes

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

$$\frac{b_7 n(\text{O}_2) - b_6 n(\text{NO})}{b_7 n(\text{O}_2) + b_6 n(\text{NO})} 2 n(\text{N}_2) J_{\text{N}_2} + P(\text{NO}) \quad (42)$$

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

Let us use the ratio

$$\frac{n(\text{NO}_y)}{n(\text{NO})} = R \quad (43)$$

in order to write (42) as follows

$$\frac{dn(\text{NO}_y)}{dt} + 2b_6 J_{\text{NO}} \cdot \frac{n^2(\text{NO}_y)}{R[b_6 n(\text{NO}_y) + R b_7 n(\text{O}_2)]} =$$

$$2 \frac{R b_7 n(\text{O}_2) - b_6 n(\text{NO}_y)}{R b_7 n(\text{O}_2) + b_6 n(\text{NO}_y)} n(\text{N}_2) J_{\text{N}_2} + P(\text{NO}) \quad (44)$$

Finally, introducing the control by eddy transport process, the continuity equation for NO_y is given by the addition of $\text{div} [n(\text{NO}_y) w(\text{NO}_y)]$ to (44). Thus, in general, we must have at any point of the stratosphere and mesosphere, the following equation pertaining to the variation of NO_y

$$\begin{aligned} \frac{\partial n(\text{NO}_y)}{\partial t} + \text{div } \Phi(\text{NO}_y) + 2b_6 J_{\text{NO}} \frac{n^2(\text{NO}_y)}{R[R b_7 n(\text{O}_2) + b_6 n(\text{NO}_x)]} = \\ 2 \frac{R b_7 n(\text{O}_2) - b_6 n(\text{NO}_y)}{R b_7 n(\text{O}_2) + b_6 n(\text{NO}_y)} n(\text{N}_2) J_{\text{N}_2} + P(\text{NO}) \end{aligned} \quad (45)$$

With this equation, it is possible to deduce the vertical distribution and the total flow of NO_y molecules.

The eddy diffusion current is given by

$$\Phi(\text{NO}_y) = n(\text{NO}_y) w(\text{NO}_y) - n(\text{NO}_y) K \left[\frac{1}{H(\text{NO}_y)} - \frac{1}{H(M)} \right] \quad (46)$$

where $w(\text{NO}_y)$ is the *vertical* diffusion velocity and K is the eddy diffusion coefficient. $H(\text{NO}_y)$ and $H(M)$ denote the NO_y and atmospheric scale height, respectively; they are given by

$$\frac{1}{H(\text{NO}_y)} = \frac{1}{n(\text{NO}_y)} \frac{\partial n(\text{NO}_y)}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z} \quad (47a)$$

and

$$\frac{1}{H(M)} = \frac{1}{n(M)} \frac{\partial n(M)}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z} \quad (47b)$$

The lower boundary conditions will be determined at the tropopause level (here 15 km) by three values of the fractional volume concentration of NO_y , namely an average value of 1×10^{-8} and minimum and maximum values corresponding to 3×10^{-9} and 3×10^{-8} , respectively.

The upper boundary conditions are determined at 100 km by a concentration of nitric oxide which may correspond to an observational value, namely 10^8 NO molecules cm^{-3} .

In order to consider various possibilities for the coefficient of vertical diffusion we have adopted two extreme conditions where the eddy diffusion coefficient varies with height, K_{MIN} and K_{MAX} , as illustrated in Fig. 4 and as used before by Nicolet and Vergison (1971) and Nicolet and Peetermans (1972).

IV. PRODUCTION OF NITRIC OXIDE AND ATOMIC NITROGEN

The production of nitric oxide molecules is given by

$$P(\text{NO}) = 2 \times 10^{10} n(\text{N}_2\text{O}) n[\text{O}(^1\text{D})] \text{ cm}^{-3} \text{ sec}^{-1} \quad (48)$$

as given by Nicolet and Peetermans (1972). The relevant numerical data involving maximum and minimum values of the concentration of ^1D oxygen atoms are summarized in Table 1. We prefer the maximum values since the photolysis of O_3 at 3130A indicates a quantum efficiency of $\text{O}(^1\text{D})$ production of about 0.5 (Simonaitis *et al.*, 1972).

As far as the production of nitrogen atoms is concerned, we may introduce several processes: First, the predissociation of N_2 in the Lyman-Birge-Hopfield bands, namely (7-0) at 1250A, (8-0) at 1226A and (9-0) at 1205A (Bates, 1954; Nicolet, 1954, 1965; Strobel, 1971) leads to a production of nitrogen atoms which is of the order of 10 atoms $\text{cm}^{-3} \text{ sec}^{-1}$ in the lower thermosphere. In fact, the most penetrating radiation corresponds to 1226A for which the absorption cross section is of the order of $5 \times 10^{-29} \text{ cm}^2$, and according to Bates (1954) and Strobel (1971), the dissociation coefficient at zero optical depth is of the order of 10^{-2} sec^{-1} .

The ionization by cosmic rays (Nicolet and Peetermans, 1972; Warneck, 1972) also leads to a production of nitrogen atoms. The average production of ion pairs [deduced from Neher (1969)] is given in Table 2 between 85 km and 35 km. This table shows that there is a large variation with latitude, almost a factor of ten between the equator and high latitudes.

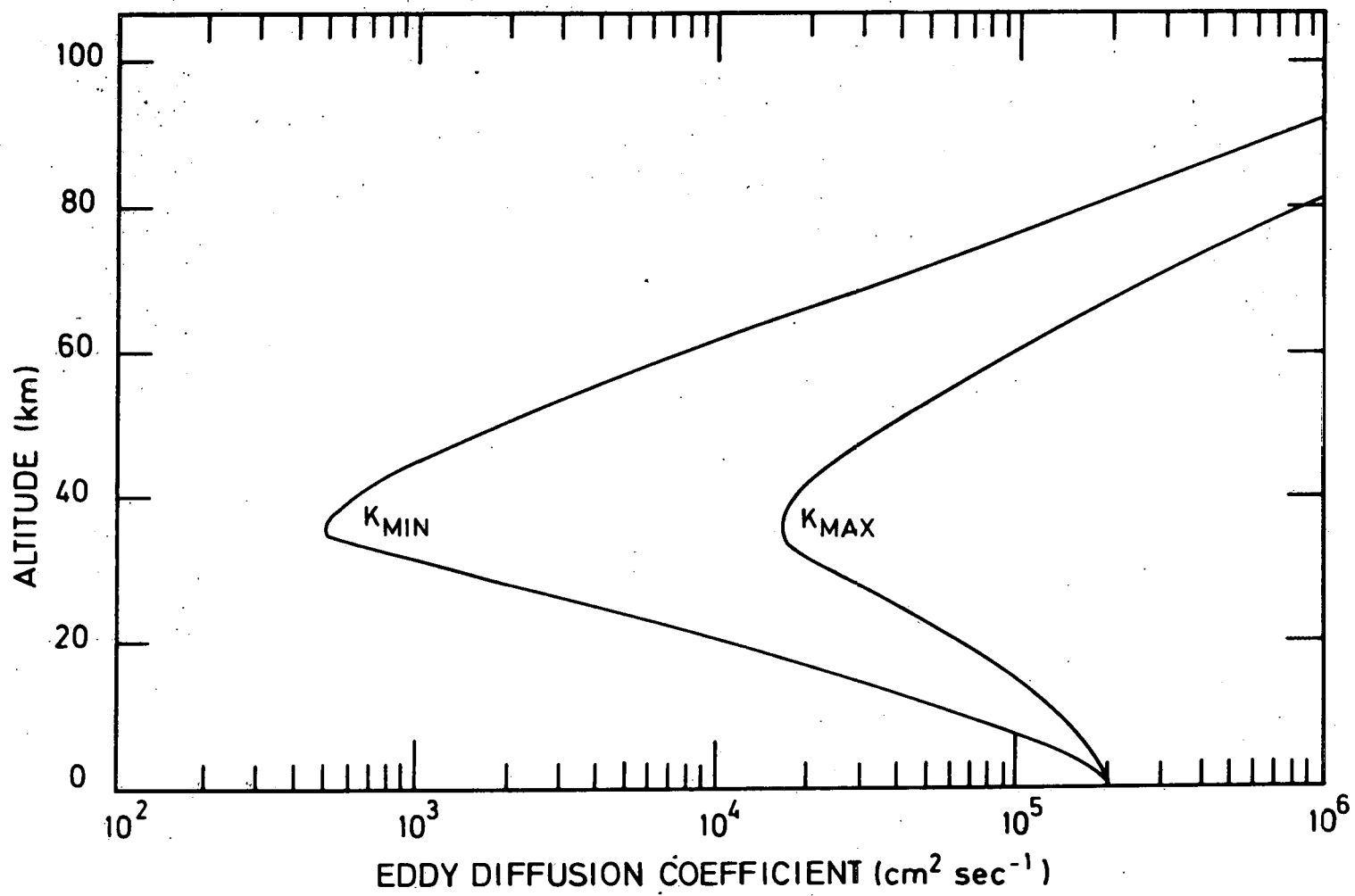


Fig. 4.- Eddy diffusion K_{MIN} and K_{MAX} adopted for the determination of vertical distribution of N_2O and transport conditions in the stratosphere and mesosphere.

TABLE 1.- Production ($\text{cm}^{-3} \text{sec}^{-1}$) of NO by oxidation of N_2O ($\text{sec}\chi = 2$)

Altitude (km)	K_{MAX}		K_{MIN}	
	$\text{O}(^1\text{D})_{\text{MAX}}$	$\text{O}(^1\text{D})_{\text{MIN}}$	$\text{O}(^1\text{D})_{\text{MAX}}$	$\text{O}(^1\text{D})_{\text{MIN}}$
15	9	4	9	4
20	37	17	36	16
25	72	42	65	38
30	112	82	60	44
35	107	93	5	4
40	45	43	9×10^{-1}	9×10^{-1}
50	1	1	2×10^{-2}	2×10^{-2}

TABLE 2.- Ion production by cosmic rays (Mean value ; $\text{cm}^{-3} \text{sec}^{-1}$)

Altitude (km)	Geomagnetic latitudes			
	0°	30°	50°	70°
85	3.4×10^{-4}	6.0×10^{-4}	1.7×10^{-3}	2.8×10^{-3}
80	8.2×10^{-4}	1.5×10^{-3}	4.2×10^{-3}	6.8×10^{-3}
75	1.8×10^{-3}	3.3×10^{-3}	9.3×10^{-3}	1.5×10^{-2}
70	3.8×10^{-3}	6.9×10^{-3}	2.0×10^{-2}	3.2×10^{-2}
65	7.4×10^{-3}	1.3×10^{-2}	3.8×10^{-2}	6.2×10^{-2}
60	1.4×10^{-2}	2.4×10^{-2}	7.0×10^{-2}	1.1×10^{-1}
55	2.5×10^{-2}	4.3×10^{-2}	1.2×10^{-1}	2.0×10^{-1}
50	4.4×10^{-2}	7.9×10^{-2}	2.2×10^{-1}	3.7×10^{-1}
45	8.1×10^{-2}	1.5×10^{-1}	4.1×10^{-1}	6.7×10^{-1}
40	1.5×10^{-1}	2.8×10^{-1}	7.9×10^{-1}	1.3
35	3.2×10^{-1}	5.6×10^{-1}	1.6	2.6

It is clear that in the whole mesosphere the ionization production, which can play a role in the lower D region, is not important for the dissociation process of molecular nitrogen. As far as solar activity is concerned, its effect is particularly important for geomagnetic latitudes greater than 50° ; there is almost a factor of 2 between minimum and maximum solar conditions (see fig. 5a). At the stratopause, the ion production is more than 1 at high geomagnetic latitudes ($> 50^\circ$).

The galactic cosmic radiation which is essentially isotropic as observed on the Earth is modulated by the interplanetary magnetic field. Thus the primary cosmic radiation that reaches the Earth is minimum at periods of maximum solar activity. Its composition which is about 83% protons, 12% alpha particles and 1% of other elements leads to an ionization principally by protons which appears under different forms. Warneck (1972) has made an estimation of a total yield of odd nitrogen corresponding to 1/3 for each ion pair produced by cosmic rays. It is known that the secondary electrons ejected by the proton ionization (see for example, Dalgarno, 1967) produce much of the ionization. If a part of the electron impact ionization corresponds to positive ions N_2^+ and O_2^+ , dissociative ionization (Rapp *et al.*, 1965) and dissociative excitation (Mumma and Zipf, 1971) also occurs leading, for example, to N^+ and N. However, the dissociative excitation is only a fraction of the total ionization (cross section less than 10^{-17} cm^2) while the dissociative ionization is of the order of 20 to 30% of the total ionization; the maximum cross section for N_2 only reaches $6 \times 10^{-17} \text{ cm}^2$. If the result published by Winters (1966) on the dissociation cross section of N_2 for electron energy from 0 to 300 eV is accepted, the total dissociation cross section for nitrogen is greater than $1.5 \times 10^{-16} \text{ cm}^2$ for electron energies from about 40 to 280 eV with a maximum value of $2 \times 10^{-16} \text{ cm}^2$ at an electron energy of about 90 eV. Comparison of such data with the cross sections for dissociative ionization published by Rapp *et al.* (1965) indicates that the dissociative ionization corresponds to about 1/3 of the total dissociation. Thus, there is a possibility to consider that the number of nitrogen atoms, which come from the dissociation of N_2 due to the impact of electrons produced by the primary ionization of cosmic rays, is of the order of the number of the ion pairs produced at the same altitude. If such dissociation process is accepted, it is clear that the production of nitrogen atoms is important at high latitudes ($\Phi > 60^\circ$). A summary of observational data (Neher, 1971) is illustrated in Fig. 5b where two curves show the vertical distribution of the ion pairs produced at Thule, Greenland, between 5 and 25 km. Peaks between 30 and 40 ion pairs are

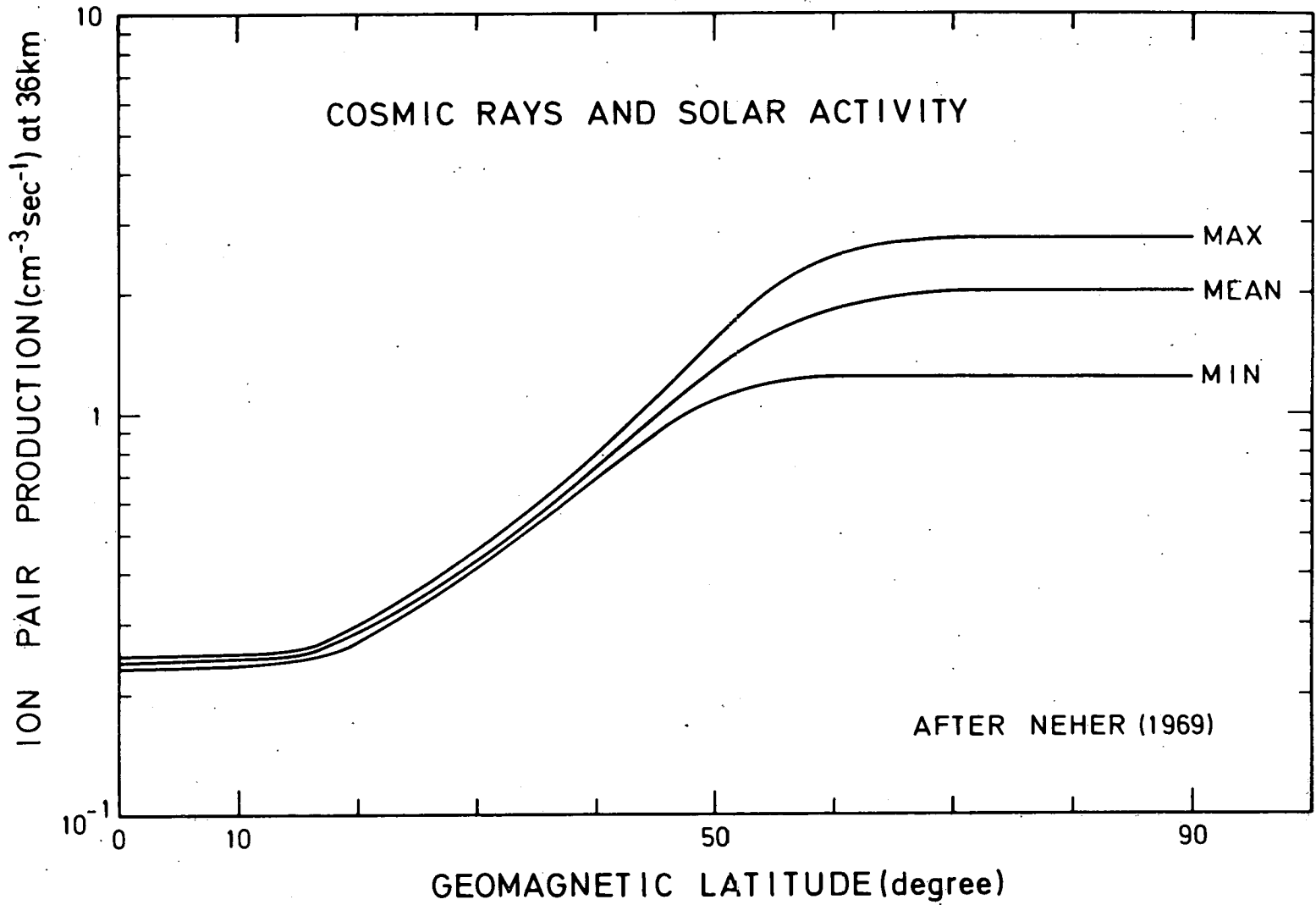


Fig. 5a.- Ion pair production versus geomagnetic latitude by cosmic rays depending on solar activity : Max for minimum solar activity and Min for maximum solar activity.

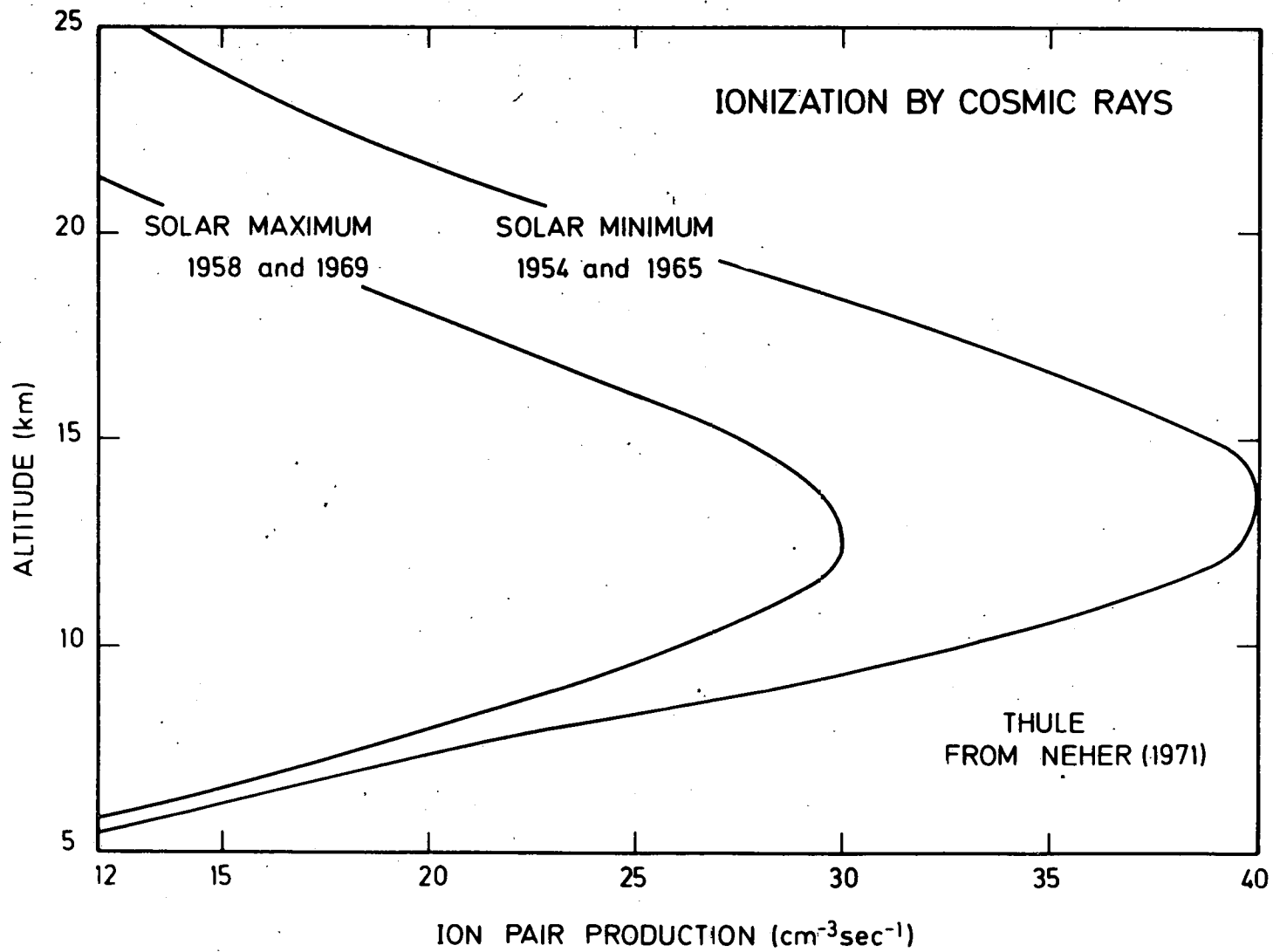


Fig. 5b.- Ion pair production in the troposphere and stratosphere at high latitudes (Thule, Greenland), for minimum and maximum solar conditions.

produced in the low stratosphere at around 12 km and 14 km, respectively. An equivalent production of nitrogen atoms (50% of the total ionization of N_2 corresponding to an identical dissociation of that molecule) is certainly more important than the photochemical production of NO from N_2O at high latitude during the winter. On the other hand, the dissociation of N_2 is less important than the production of NO at low latitudes. For that reason, we have not introduced the production of nitrogen atoms by cosmic rays in all computations and we use here a conventional production as given in Table 2 and a few examples will be given with a production $P(N) = 1$ or $10 \text{ cm}^{-3} \text{ sec}^{-1}$ in order to show the real effect of an atomic nitrogen production.

Finally, we may add that there is a possibility of an increase, in the D region, of the production of nitrogen atoms due to special solar effects such as resulting from solar flares and corpuscular radiation penetrating into the D region. A special study is required for each case. But we consider that such additional effects cannot change the general conclusion even if they may disturb the normal distribution of nitric oxide in the mesosphere.

V. NITRIC OXIDE AND OTHER NITROGEN OXIDES

The steady-state continuity equation which is used for the mesosphere and stratosphere is, from (45),

$$\frac{\partial \Phi(\text{NO}_x)}{\partial z} + \frac{2 J_{\text{NO}} b_6 n^2(\text{NO}_y)}{R [R b_7 n(\text{O}_2) + b_6 n(\text{NO}_y)]} = P(\text{NO})$$

$$+ 2n(\text{N}_2) J_{\text{N}_2} \frac{R b_7 n(\text{O}_2) - b_6 n(\text{NO}_y)}{R b_7 n(\text{O}_2) + b_6 n(\text{NO}_y)} \quad (49)$$

where $P(\text{NO})$ (see Nicolet and Peetermans, 1973), calculated by (48) as given in Table 1, is illustrated in Fig. 6 for a solar zenith angle 60° ; $2n(\text{N}_2) J_{\text{N}_2}$ will be arbitrarily taken 0, 1 and $10 \text{ cm}^{-3} \text{ sec}^{-1}$ in order to make various comparisons.

To solve (49) we have prescribed, as indicated before, an upper boundary condition with $n(\text{NO}) = 10^8 \text{ cm}^{-3}$ at 100 km which may represent an average observational value (Meira, 1971).

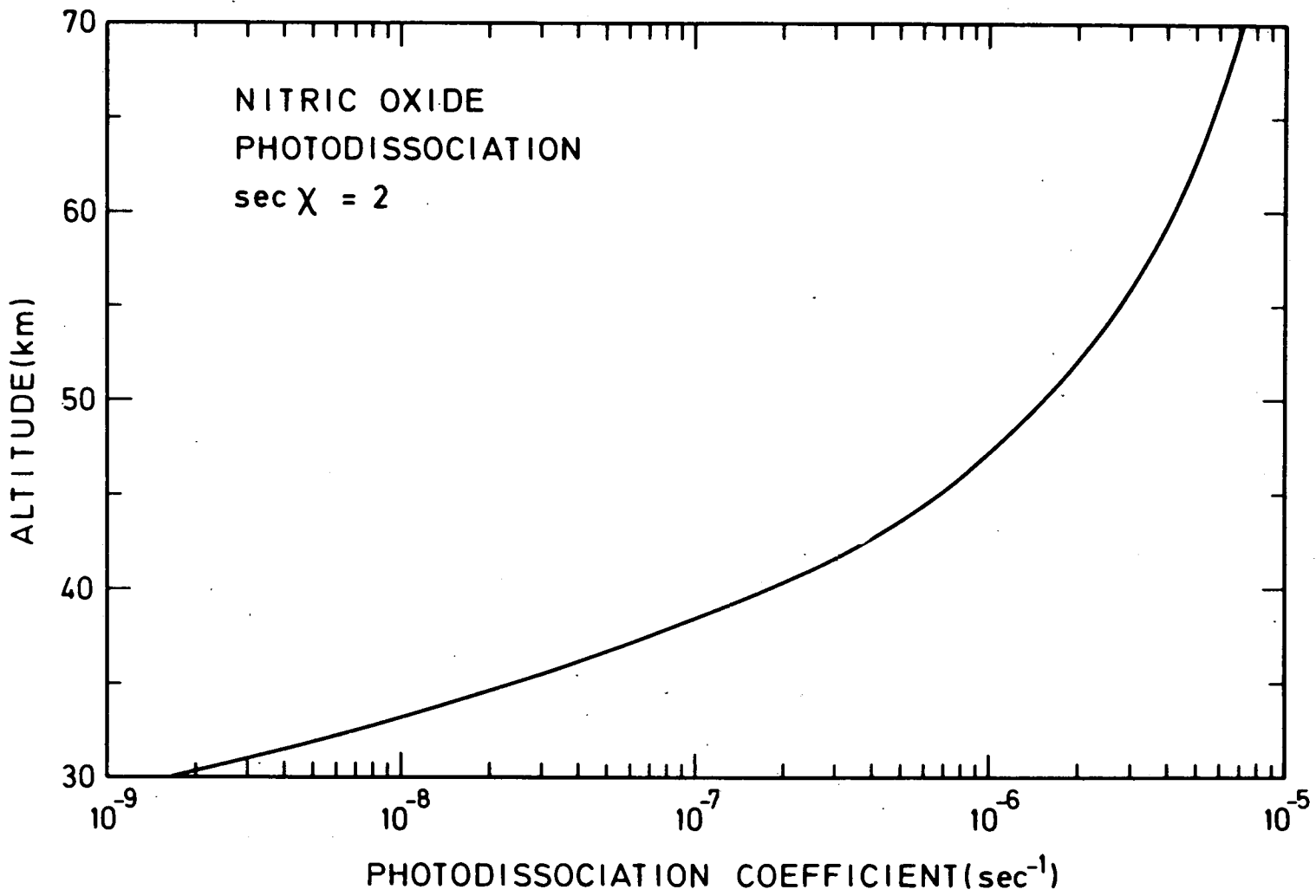


Fig. 6.- Photodissociation coefficient of nitric oxide for a solar zenith angle of 60°.

At the lower boundary, which corresponds to the tropopause, the appropriate condition is more difficult to prescribe since there are different tropopauses versus latitude. Here we have taken as NO_y fractional volume concentration an average value of 1×10^{-8} at 15 km and as indicated before two other extreme values 3×10^{-9} and 3×10^{-8} .

We have explored the effect of the photodissociation of NO compared to a model where NO is not subject to dissociation in the lower thermosphere and mesosphere. It is clear from Fig. 7, which shows the effect of dissociation, that the photodissociation process leads to a rapid decrease of the nitric concentration in the mesosphere. From results illustrated in Fig. 8 where additional productions of atomic nitrogen of $1 \text{ atom cm}^{-3} \text{ sec}^{-1}$ and $10 \text{ atoms cm}^{-3} \text{ sec}^{-1}$ are considered, it can be deduced that such productions are too low in the lower stratosphere to affect the vertical distribution of nitric oxide which only depends in the value of the eddy diffusion coefficient. But, in the mesosphere, there is a minimum between 80 and 70 km which is strongly related to the production of atomic nitrogen particularly when the eddy diffusion coefficient is taken with a too low value. When K_{MAX} is adopted, the NO concentration strongly depends on transport conditions and not very much on the production of nitrogen atoms. Since turbulence in the mesosphere must lead to a fairly high value of the eddy diffusion coefficient, it is possible to consider that concentrations of NO between 10^6 and 10^7 molecules cm^{-3} near 70 km are more realistic than low values of $n(\text{NO})$ between 10^5 and 10^6 molecules cm^{-3} . Such results explain why nitric oxide was not observed by Jursa *et al* (1959) between 63 and 87 km; the NO concentration is less than 10^8 cm^{-3} . Nevertheless, if we consider the possibility of a very high eddy diffusion coefficient in the whole mesosphere such as values of the order of $10^6 \text{ cm}^2 \text{ sec}^{-1}$ at 100 km, $10^7 \text{ cm}^2 \text{ sec}^{-1}$ at 90 km, $10^6 \text{ cm}^2 \text{ sec}^{-1}$ at 60 km and $10^5 \text{ cm}^2 \text{ sec}^{-1}$ at 50 km (Zimmerman, private communication) the NO profile in the mesosphere is modified since it is very sensitive to eddy diffusion coefficient. In any case, it seems that it is not possible to reach NO concentrations greater than 10^8 cm^{-3} .

In the stratosphere (Fig. 9), there is a peak of the vertical distribution of the mixing ratio of NO_y which is related to the production peak of NO. Its value depends more on the production rate than on the lower boundary condition which has been assumed at the tropopause level. There is a difference in the upper stratosphere between K_{MIN} and K_{MAX}

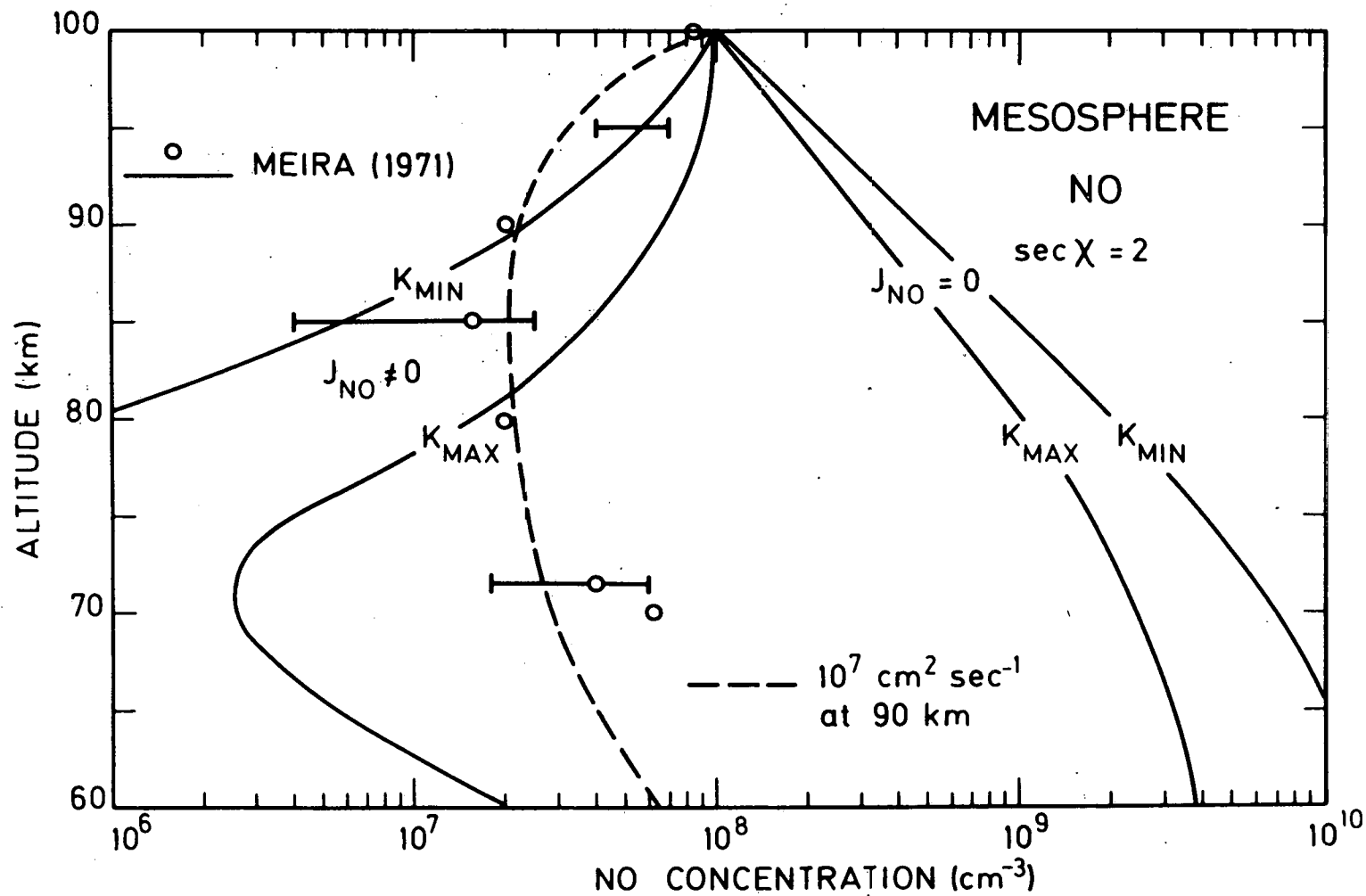


Fig. 7.- Theoretical nitric oxide concentration profile for a variety of conditions. $J_{\text{NO}} = 0$ would correspond to a model where photodissociation of nitric oxide is neglected. $J_{\text{NO}} \neq 0$ corresponds to an exact vertical distribution of the photodissociation of nitric oxide with two conventional conditions K_{MIN} and K_{MAX} and a very high eddy diffusion coefficient (dotted line).

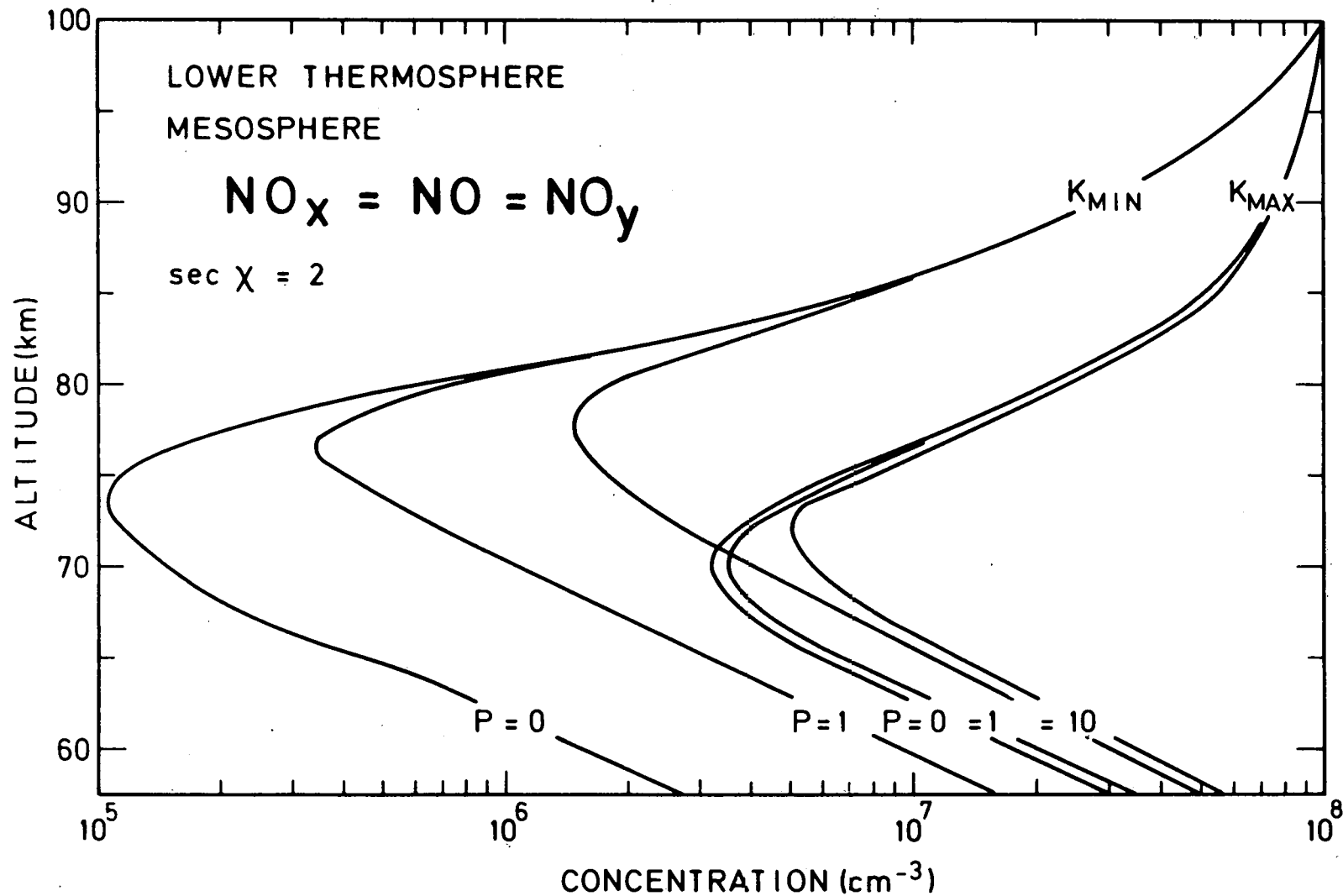


Fig. 8.- Vertical distribution of the concentration of nitric oxide in the lower thermosphere and mesosphere according to different transport conditions K_{MIN} and K_{MAX} and various productions of nitrogen atoms $P(\text{N}) = 0, 1$ and $10 \text{ cm}^{-3} \text{ sec}^{-1}$.

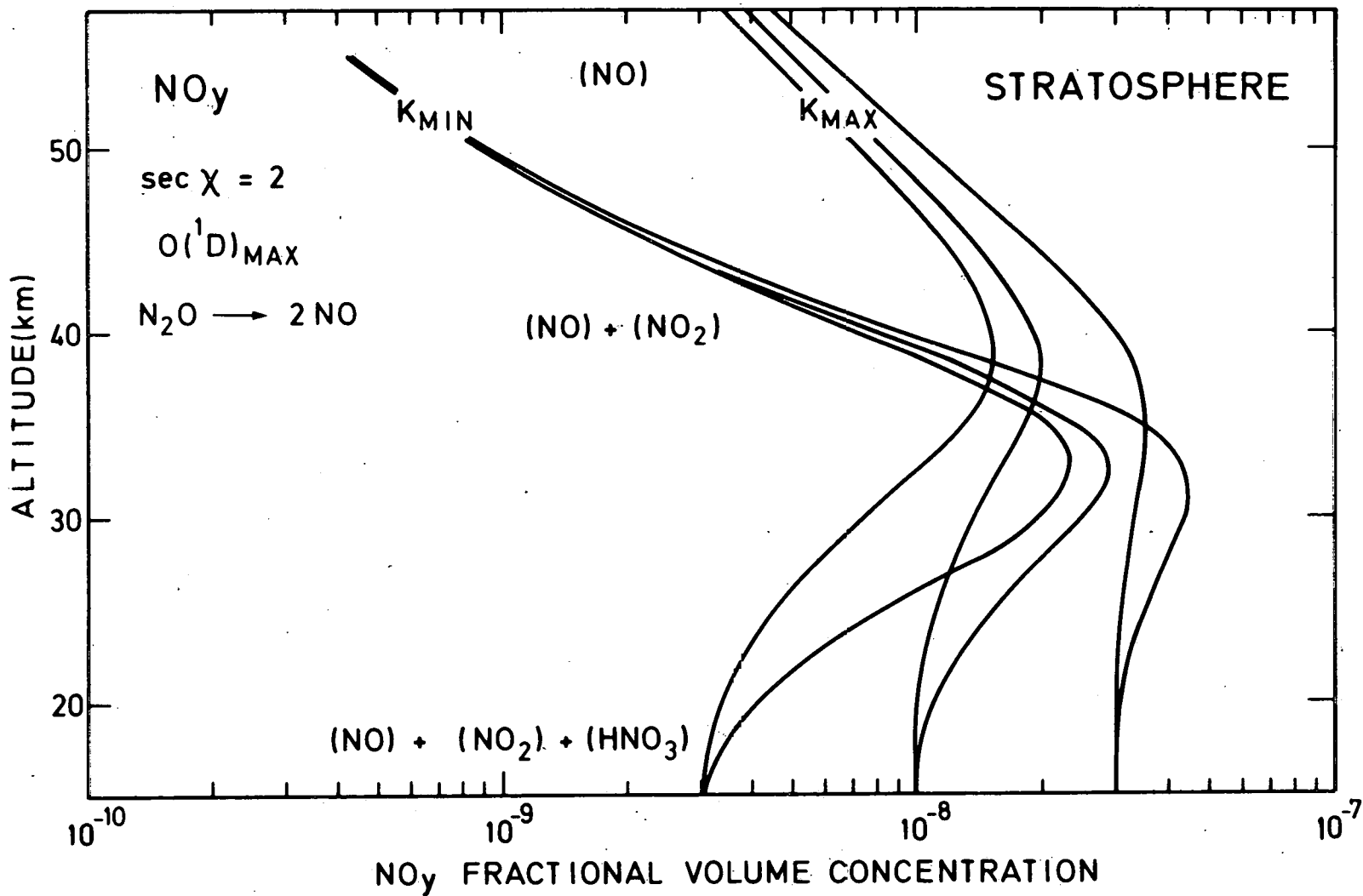


Fig. 9.- NO_y mixing ratio in the stratosphere. $\text{NO}_y = \text{NO}_x + \text{HNO}_3 = \text{NO} + \text{NO}_2 + \text{HNO}_3$. Conditions depending on the eddy diffusion coefficient.

leading to a difference of about a factor of ten in the mixing ratio or in the NO concentration (Fig. 10). NO is the principal nitrogen oxide constituent only in the upper stratosphere near the stratopause. In the middle stratosphere, it is necessary to consider NO and NO₂ with HNO₃.

When various sources of production of atomic nitrogen are added to the direct production of nitric oxide there is not too much difference in the major part of the stratosphere. The vertical distribution of the concentration of NO_y (Fig. 11) or of its fractional volume abundance (Fig. 12) are not disturbed by a source of 1 nitrogen atoms cm⁻³ sec⁻¹ or even by 10 nitrogen atoms cm⁻³ sec⁻¹ except near the stratopause for conditions of very low eddy diffusion coefficient. However, the variation which is shown near the stratopause cannot occur since it is difficult to imagine in the upper stratosphere sources of 10 nitrogen atoms cm⁻³ sec⁻¹. However, in the polar night or in high latitudes during the winter season, the production of nitrogen atoms would be equivalent to the ion pair production illustrated in Fig. 5b, if the dissociation is represented by 50% of the total ionization.

In order to see detailed effect of the production and loss process of NO, Fig. 13 and 12 include the three terms P(NO_y) the production rate of NO, L(NO_y) the loss rate and div Φ(NO_y) the transport rate related to the eddy diffusion coefficient. In Fig. 13 representing conditions for the minimum value of the eddy diffusion coefficient, K_{MIN}, the effect of the production of NO below 35 km is *counter balanced* by its transport to the troposphere. In the region between 40 and 70 km the transport would not be important since chemical equilibrium conditions can occur more rapidly. In the lower thermosphere the downward flux corresponds to the loss by photodissociation. When the eddy diffusion K_{MAX} is used in the calculation (Fig. 14) the NO production and loss rate are less sensitive to the effect of additional sources. The effect is not important in the whole stratosphere and is really negligible in the lower thermosphere. However, since a normal production of 10 nitrogen atom at 60 km cannot be accepted, the various rate of production of loss and of transport, which are indicated in Fig. 14 without additional production of nitrogen atoms, illustrate the general conditions for atmospheric conditions represented by K_{MAX}. If the atmospheric conditions are such that the maximum eddy diffusion coefficient K_{MAX} is not too far from real conditions in the mesosphere it seems that aeronomic conditions in the stratosphere require a low eddy diffusion such as K_{MIN}. The comparison of the effect of these two eddy diffusion coefficients, which is given in Fig. 15, shows how the upper stratosphere and

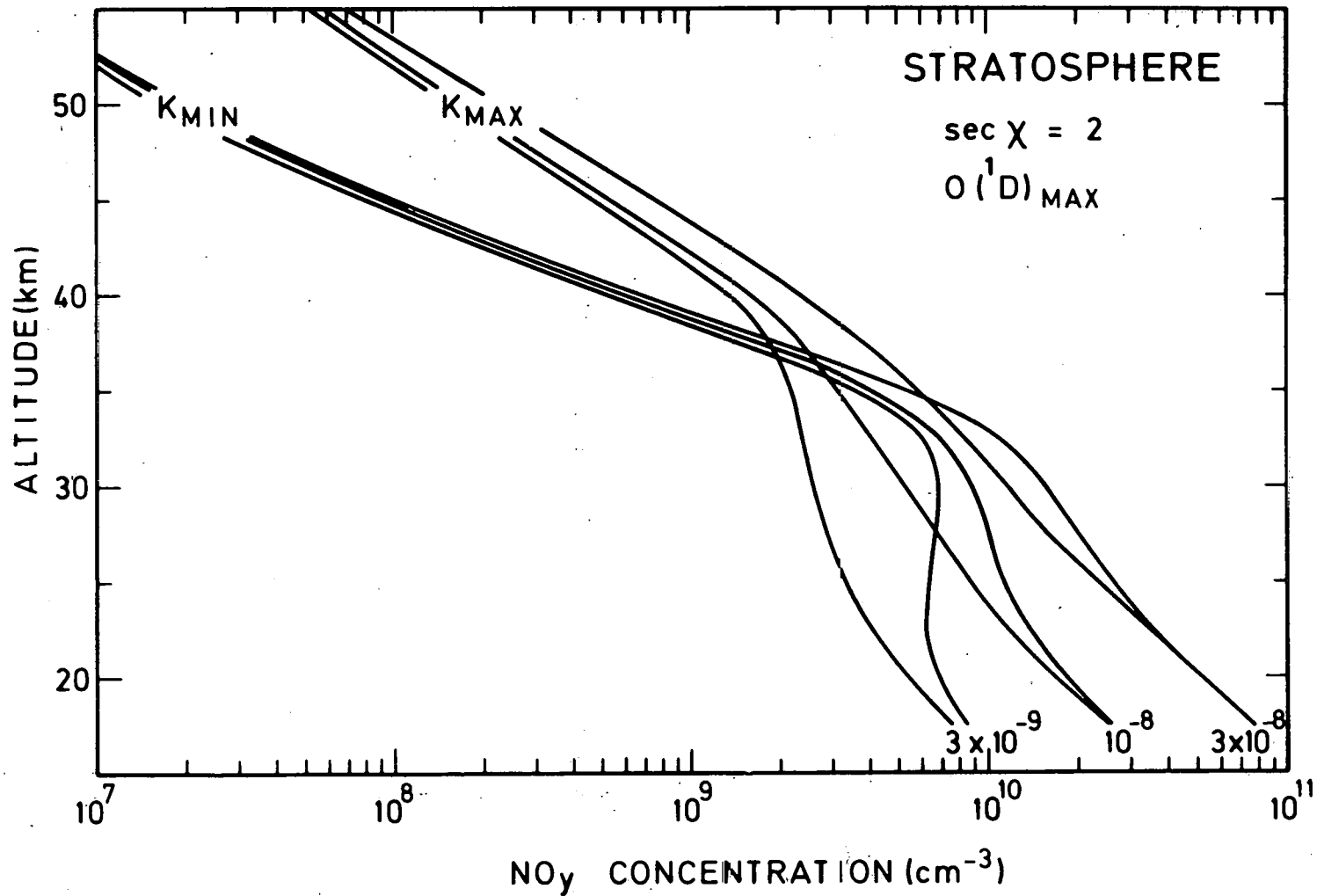


Fig. 10.- NO_y concentration in the stratosphere for two different conditions of the eddy diffusion coefficient.

$$NO_y = NO_x + HNO_3 = NO + NO_2 + HNO_3.$$

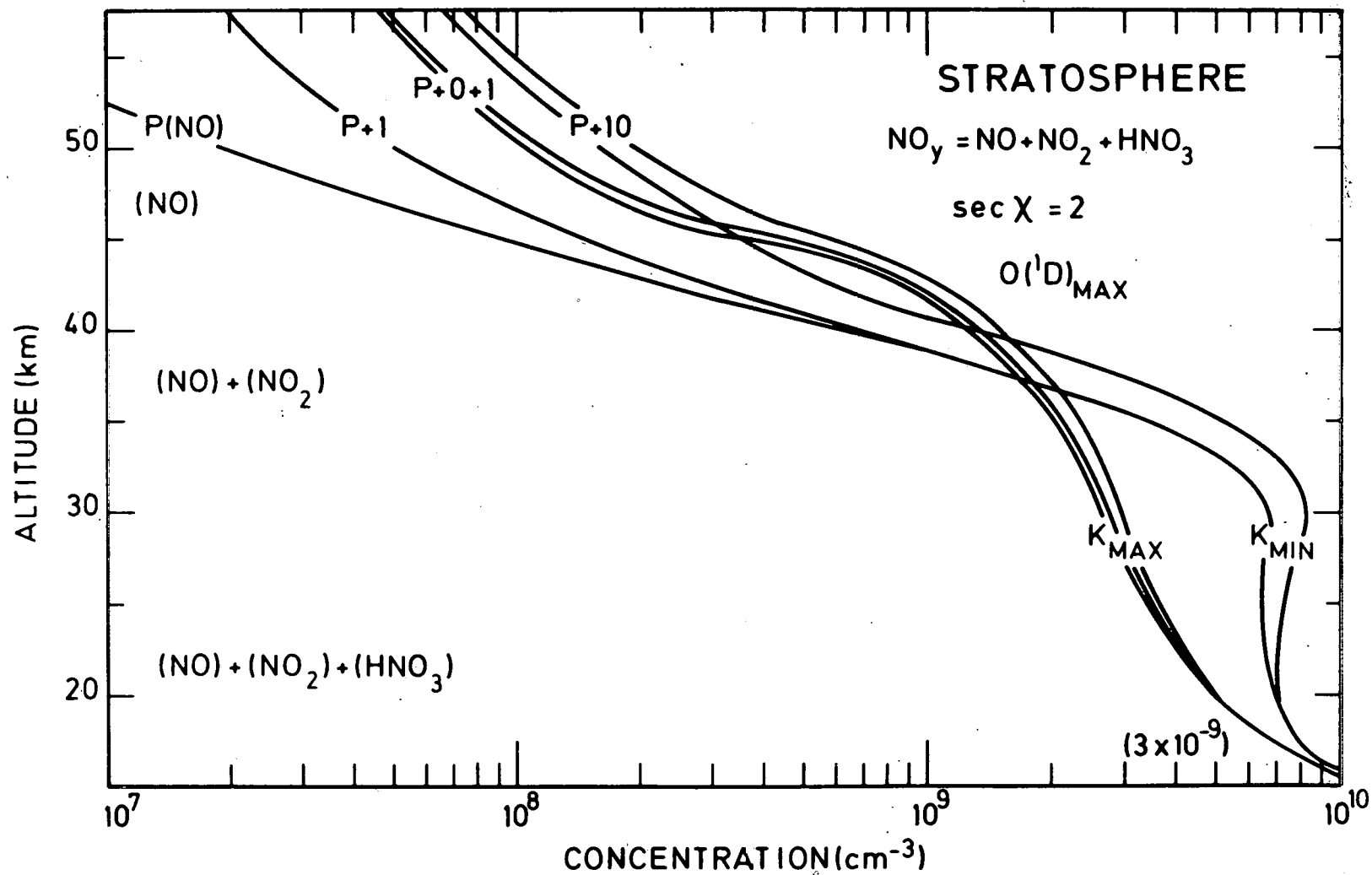


Fig. 11.- Effect of a disturbance in the stratosphere on the vertical distribution of NO_y when the mixing ratio is 3×10^{-9} at 15 km. Effect of a production of 1 or 10 nitrogen atoms $\text{cm}^{-3} \text{sec}^{-1}$.

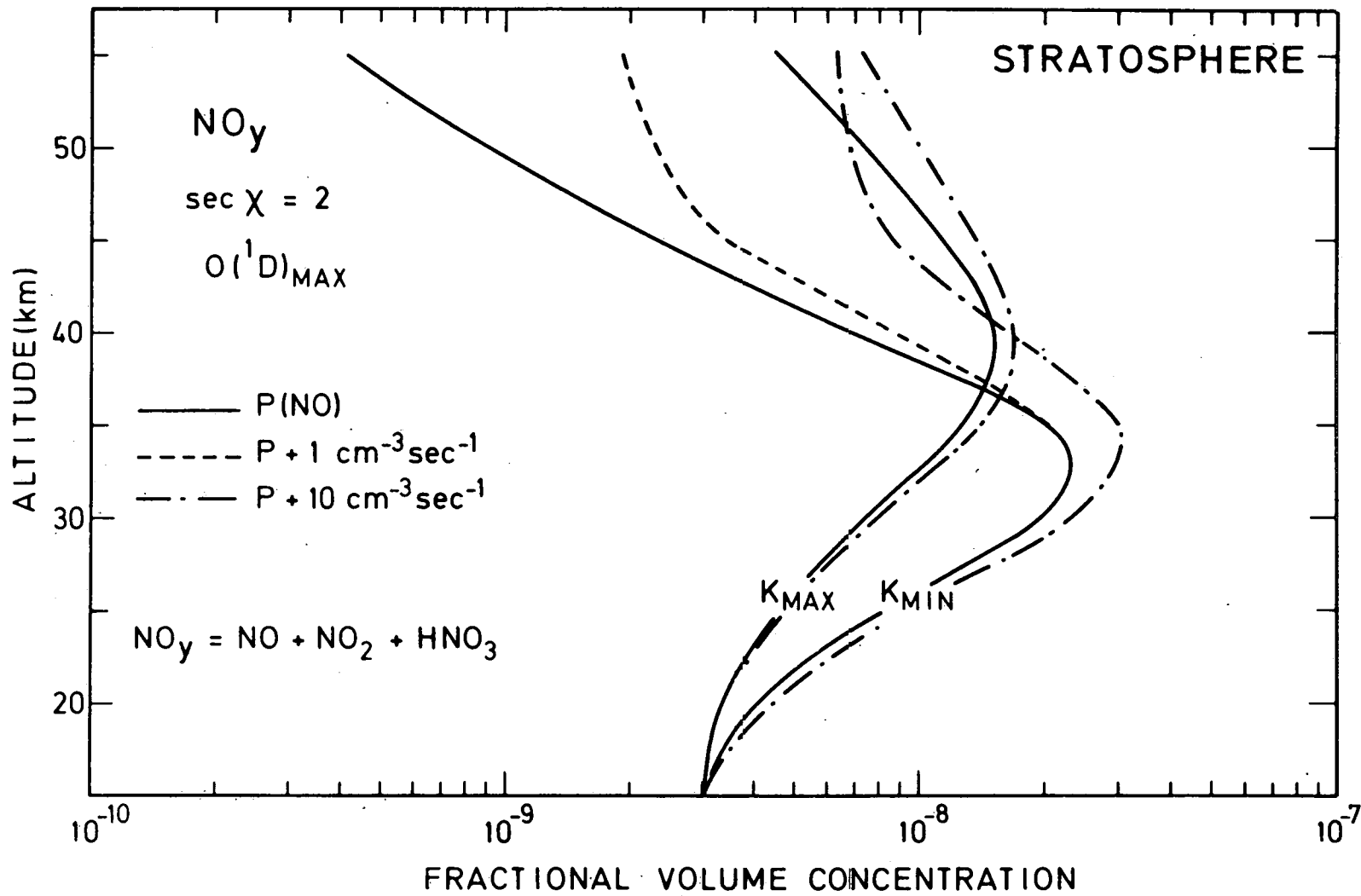


Fig. 12.- Distribution of the mixing ratio of NO_y in the stratosphere when production of nitrogen atoms is involved.

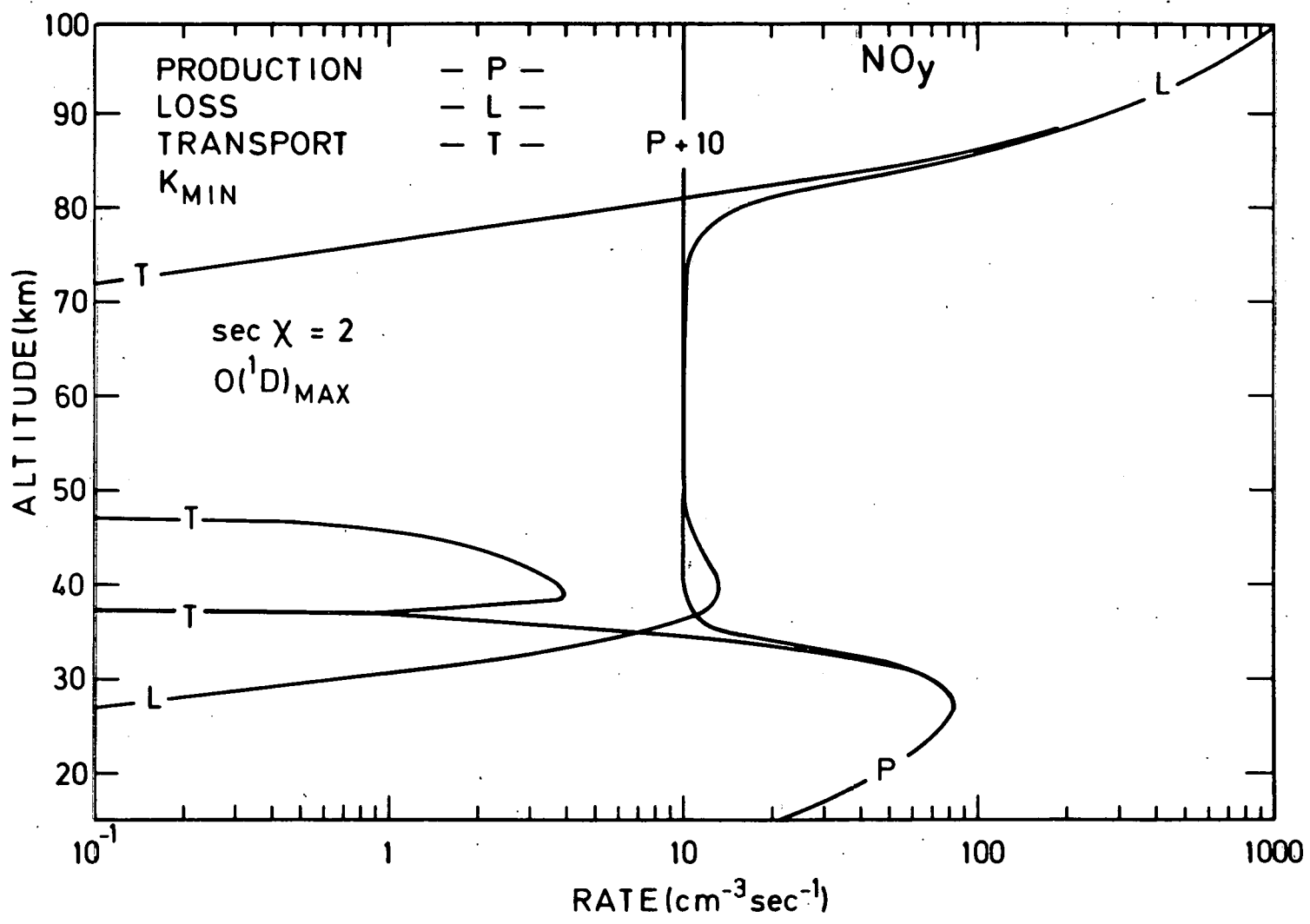


Fig. 13.- Production, loss and transport rates in the lower thermosphere, mesosphere and stratosphere if the eddy diffusion is very low. Effect of an impossible production of 10 nitrogen atoms in the upper stratosphere and lower mesosphere.

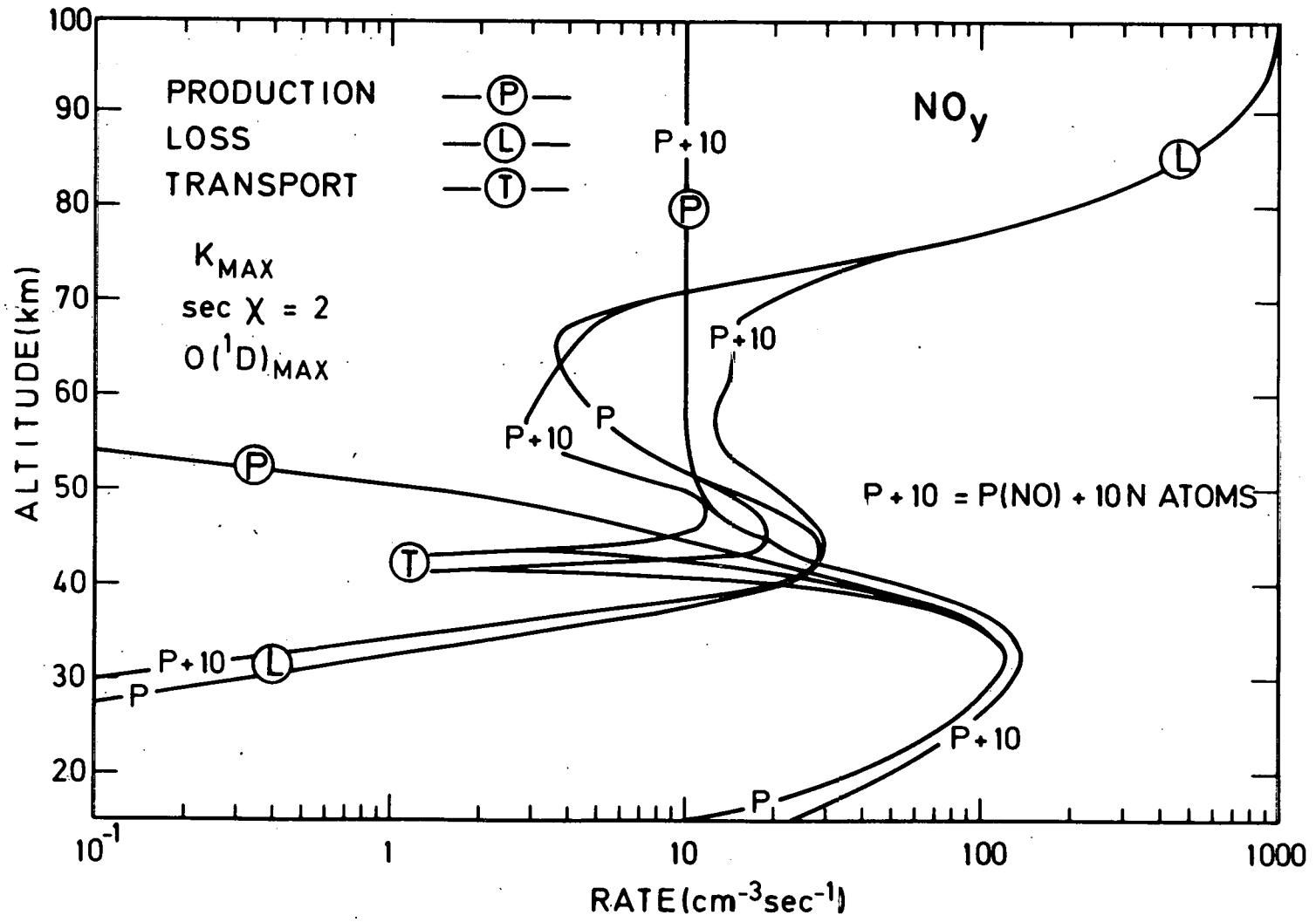


Fig. 14.- Production, loss and transport rates with a high eddy diffusion coefficient even in the stratosphere. Effect of a production of 10 nitrogen atoms is not too important.

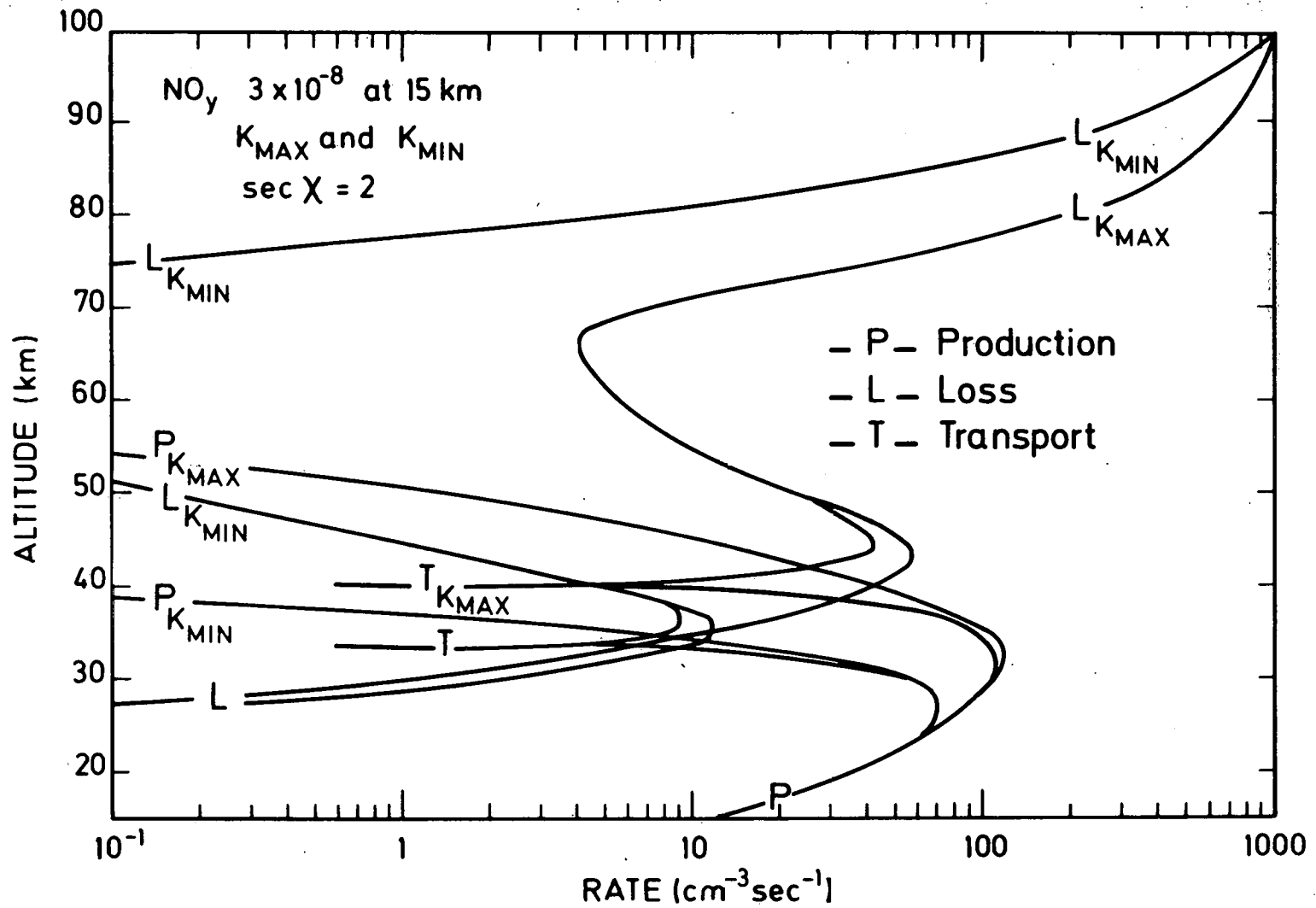


Fig. 15.- Comparison of the various rates (production, loss and transport) where two extreme eddy diffusion coefficients are considered.

the whole mesosphere are affected as far as the production and loss terms are affected when extreme values are adopted for the values of the eddy diffusion coefficients.

In Fig. 16 and 17 two examples for K_{MAX} and K_{MIN} show that the loss and transport terms are not too much affected when the lower boundary conditions are changed by a factor of ten.

If we consider the vertical distribution of each constituent HNO_3 , NO_2 and NO for a steady state represented by three different lower boundary conditions, we can see (cf. Fig. 18) the variety of profiles. The vertical distribution of the mixing ratio of HNO_3 which is shown in Fig. 18 indicates that an exact value cannot be found if the exact value of the OH radical concentration is not known with precision. Two ratios $n(HO_2)/n(OH) = 1$ and 9 show possible limits, but no clear indication can be given without more precise measurements of the rate coefficient of reactions in which OH and HO_2 are involved. However, it can be said according to the important observations of HNO_3 by Murcay *et al* (1973), that the mixing ratio in the lower stratosphere (20-25 km) which is greater than 10^{-8} requires a relatively high concentration of OH radicals. It seems, therefore, that the observed vertical distribution of nitric acid in the stratosphere must be analysed by considering an exact and relatively high concentration of OH radicals and a lower boundary condition of $n(NO_y)/n(M) > 3 \times 10^{-9}$. Furthermore, when the lower boundary condition is fixed, the values adopted of the eddy diffusion coefficient do not play the essential role (see Fig. 19) in the vertical distribution of HNO_3 ; again the absolute value of the OH radical concentration is important.

In order to show the differences occurring between the vertical distributions of NO , NO_2 and HNO_3 in the stratosphere, Fig. 20 shows their mixing ratio for two different values of the ratio $n(HO_2)/n(OH)$ when the lower boundary condition at 15 km is $n(NO_y)/n(M) = 10^{-8}$. Nitric acid plays the leading role in the lower stratosphere, nitrogen dioxide reaches a peak near 35 km and even if the mixing ratio of nitric oxide decreases in the upper stratosphere its concentration is greater than that of NO_2 and HNO_3 together.

Fig. 21 is an example of the possibility to obtain a very low mixing ratio of nitric oxide in the lower stratosphere; in order to reach mixing ratios less than 10^{-9} near 20 km, the

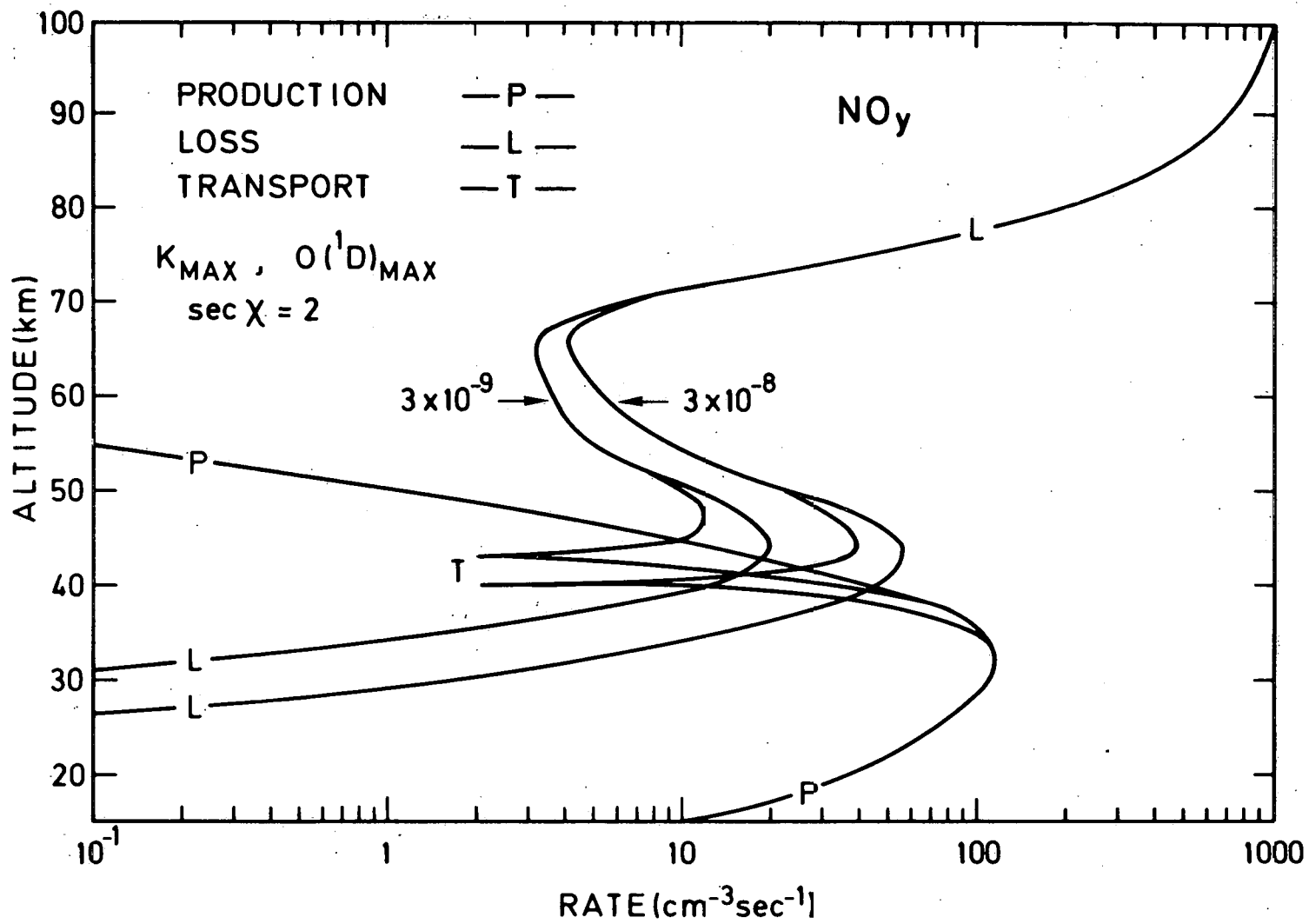


Fig. 16.- Effect of the lower-boundary conditions on the various rates (loss and transport term). Without great importance.

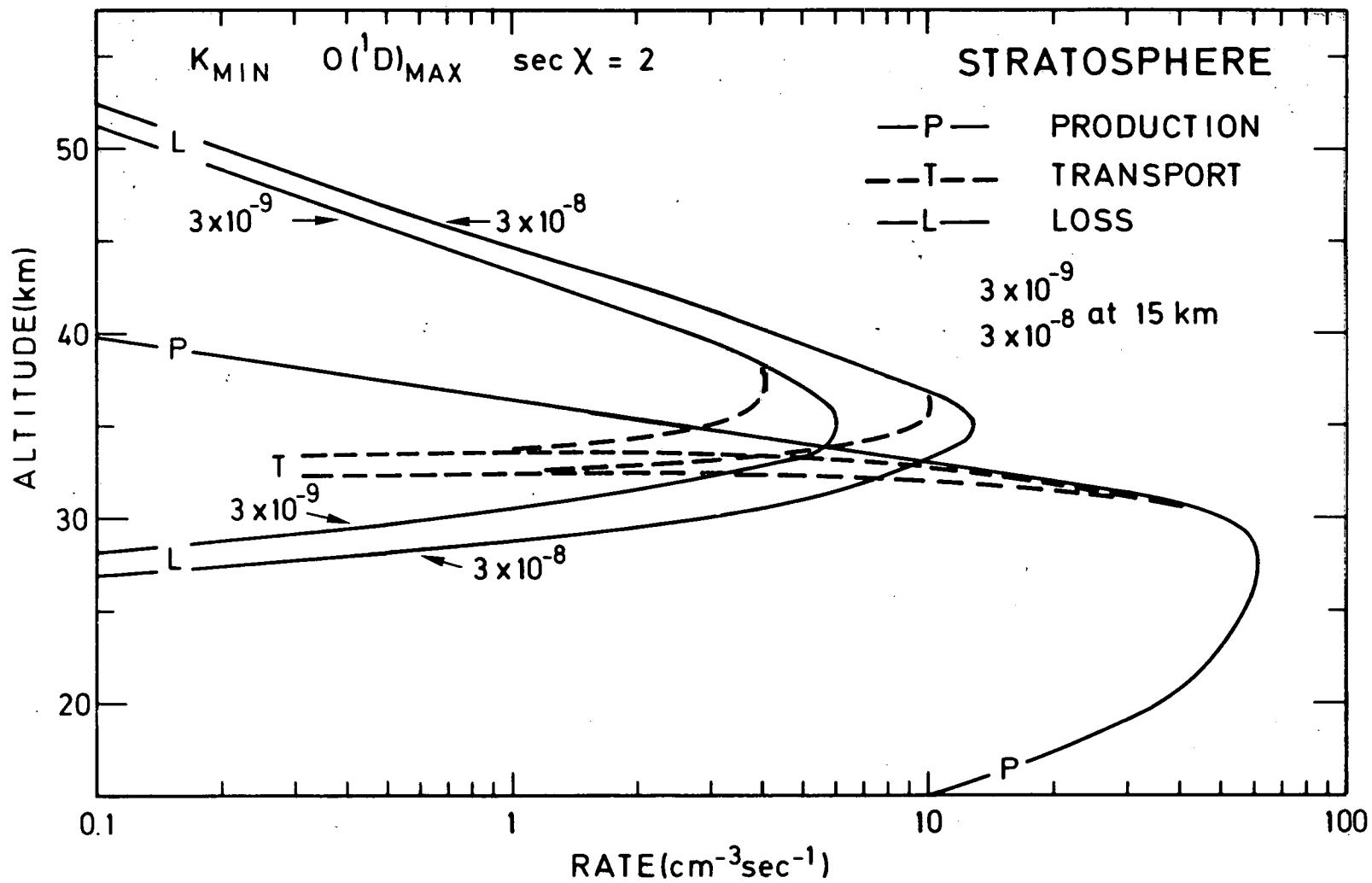


Fig. 17.- Production, transport and loss rates which can be considered as the most probable in the stratosphere. The production term may increase in the lower part of the stratosphere by the cosmic ray effect.

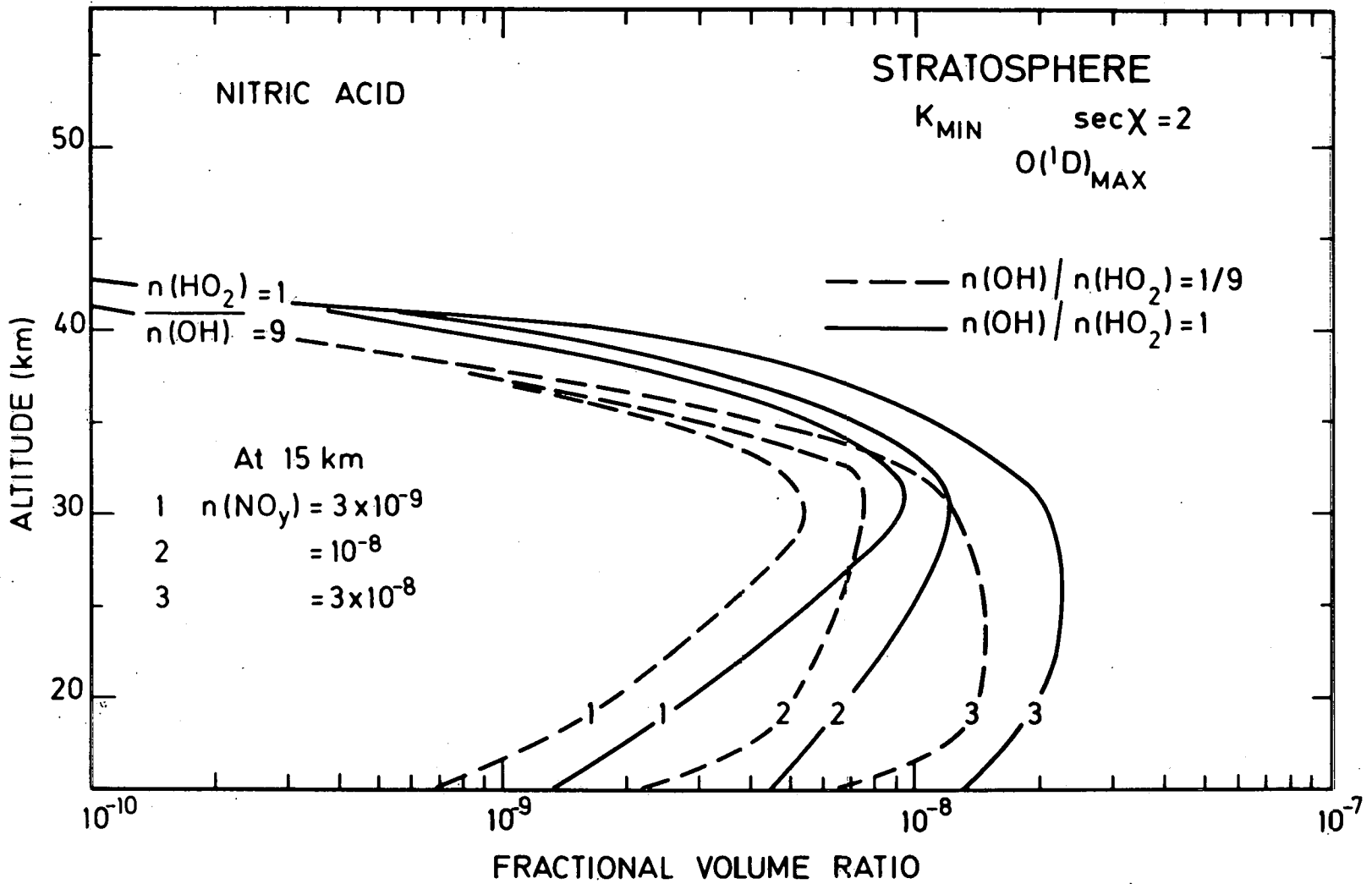


Fig. 18.- Mixing ratio of nitric acid in the stratosphere for various conditions : three different lower boundary conditions $n(\text{NO}_y)/n(\text{M}) = 3 \times 10^{-9}$, 10^{-8} and 3×10^{-8} and two different ratios $n(\text{HO}_2)/n(\text{OH}) = 1$ and 9.

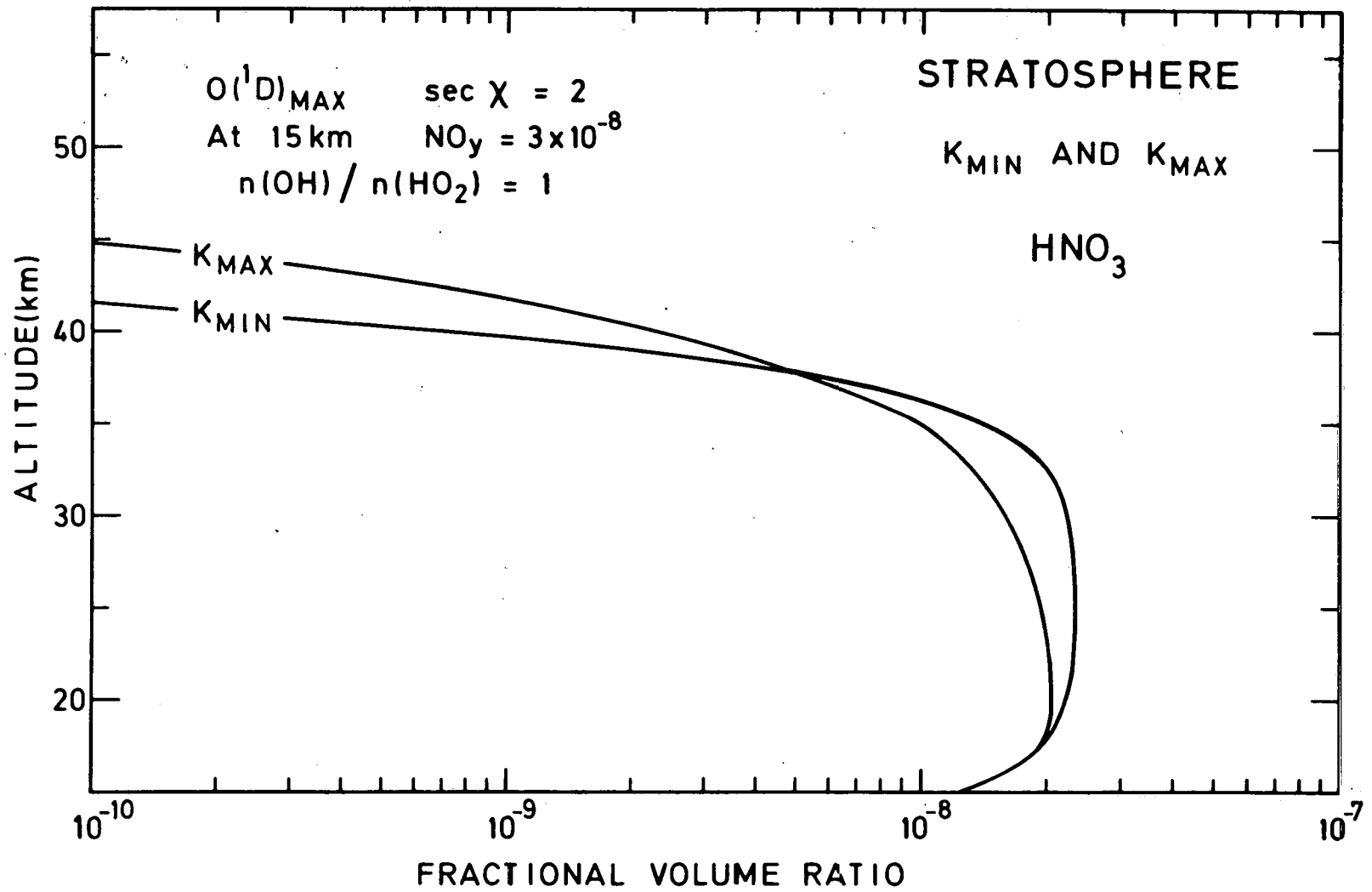


Fig. 19.- Mixing ratio of nitric acid in the stratosphere for two different eddy diffusion coefficients. Effect is not important.

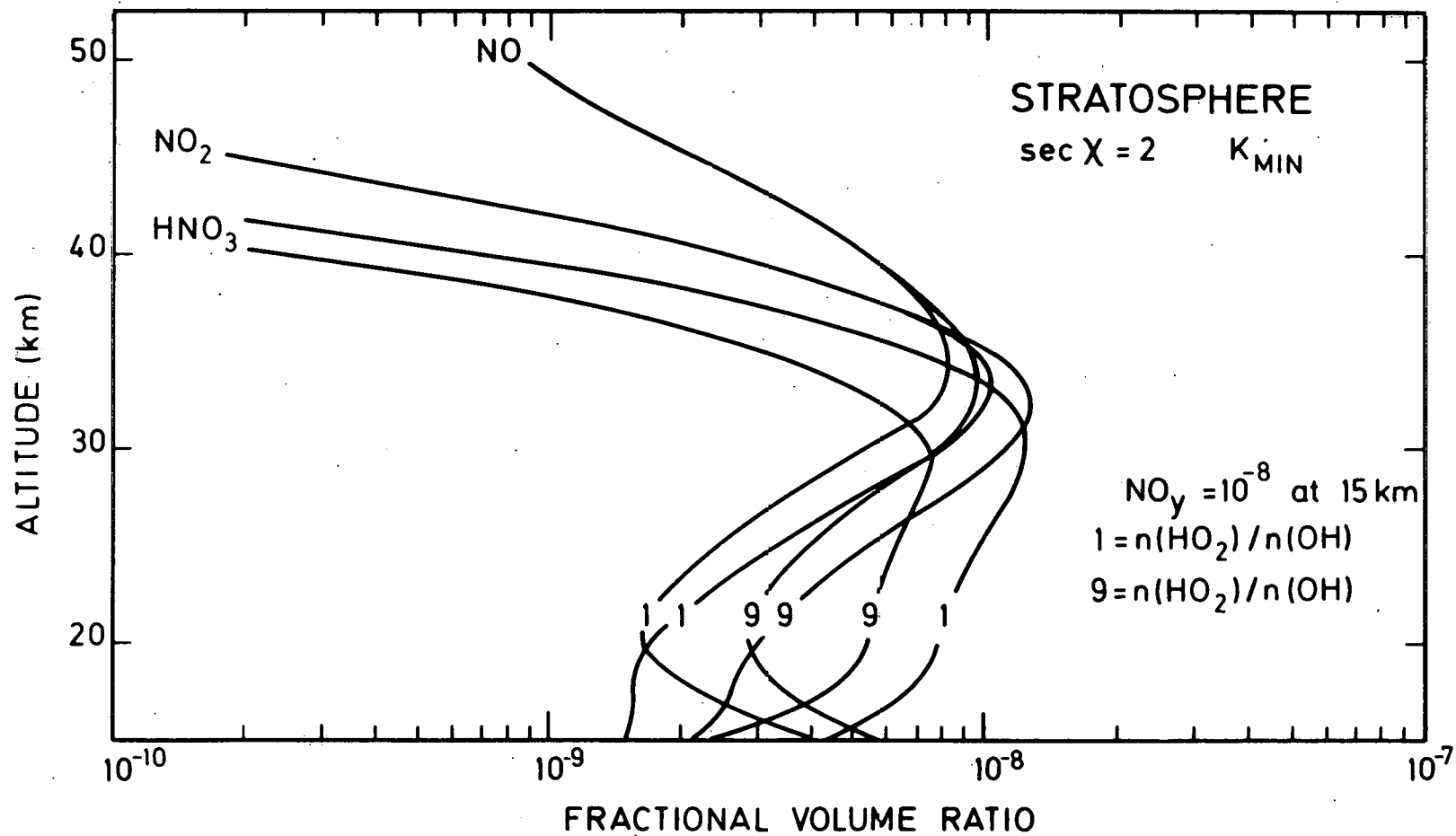


Fig. 20.- Mixing ratios of HNO_3 , NO_2 and NO when $\text{NO}_y = 10^{-8}$ at 15 km for two different values of the ratio $n(\text{OH})/n(\text{HO}_2)$.

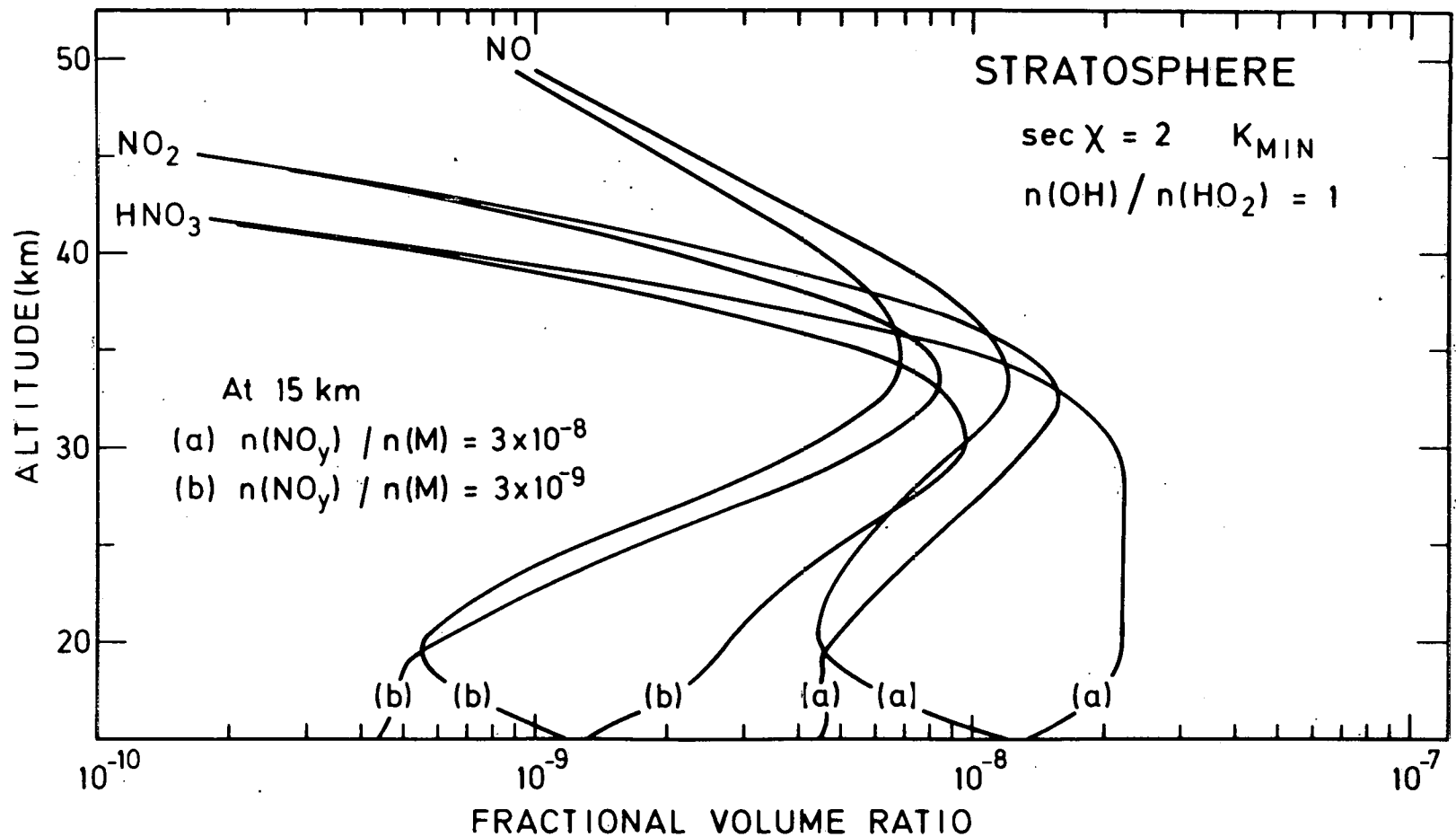


Fig. 21.- Mixing ratio of HNO₃, NO₂ and NO for two different lower boundary conditions at 15 km and a fixed ratio for n(OH)/n(HO₂).

total mixing ratio (NO_y) cannot be more than 10^{-8} at 15 km. The lower boundary conditions play a role in the vertical distribution of NO, NO_2 and HNO_3 up to the peak of their mixing ratios between 30 and 40 km. In the upper stratosphere the vertical distribution is independent of the lower boundary conditions but only depends on the diffusion coefficient.

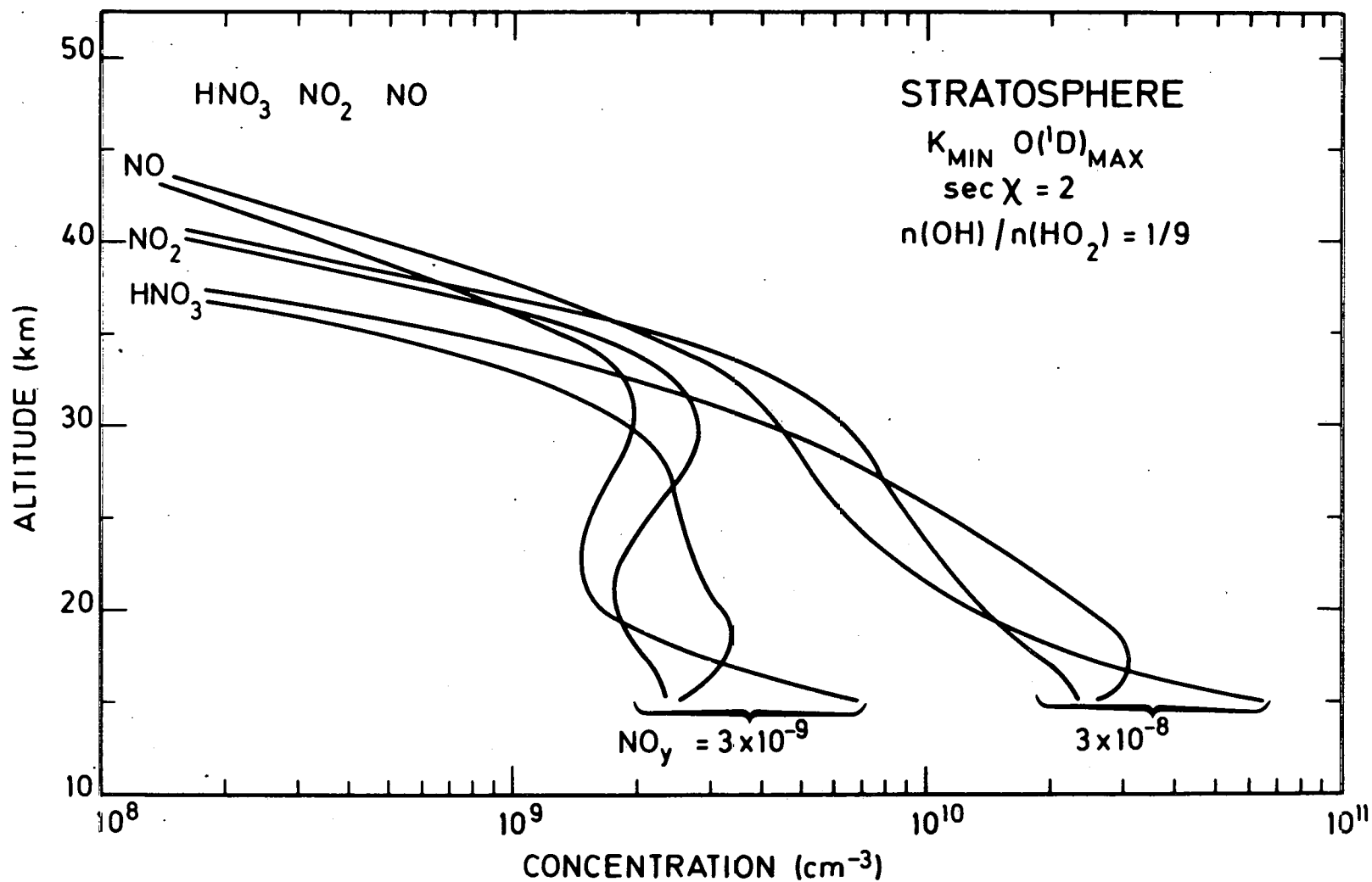
Fig. 22 and 23 illustrate the vertical distribution of the concentrations of nitric acid, nitrogen dioxide and nitric oxide in the stratosphere for two different lower boundary conditions, namely a minimum value for the mixing ratio of $\text{NO}_y = 3 \times 10^{-9}$ and a high value $\text{NO}_y = 3 \times 10^{-8}$. The differences between the results shown in Fig. 22 and 23 correspond to the differences between the ratios $n(\text{HO}_2)/n(\text{OH}) = 9$ and 1, respectively. The adopted concentration of the hydroxyl radicals are given in Table 3 according to Nicolet and Peetermans (1973).

It can be said that the various concentrations are very sensitive to the values of the OH radical concentrations. An increase in the absolute values of the nitric acid concentrations is obtained when there is a decrease in those of nitrogen dioxide and nitric oxide concentrations. In other words, an increase of the water vapor in the stratosphere leads to a decrease of nitric oxide and nitrogen dioxide.

Finally, it is easy to see that the transport which is involved in the mesosphere and stratosphere corresponds to downward fluxes in the lower thermosphere and mesosphere and in the lower stratosphere. In the lower mesosphere and upper stratosphere (fig. 24) there is a small upward current. In the thermosphere and mesosphere the transport is due to NO which comes from the E region where it is formed. There is no possibility to have a downward current of nitric oxide from the mesosphere into the stratosphere. In the lower stratosphere the downward current is mainly due to nitric acid which after crossing the tropopause disappears in the troposphere.

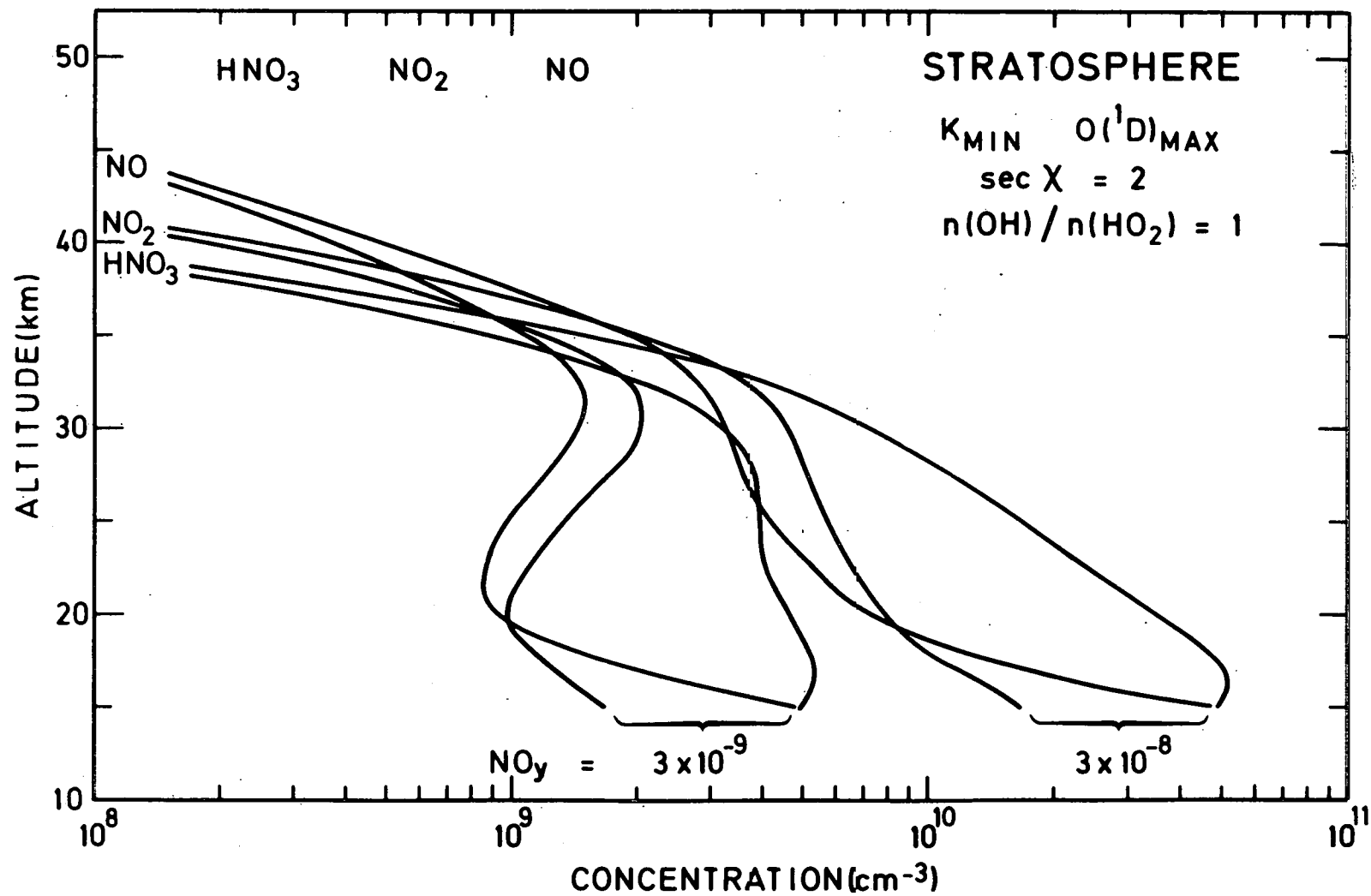
VI. SUMMARY

The essential reactions in which nitrogen oxides are involved in the chemosphere not only depend on the oxygen atmosphere (ozone and oxygen atoms) but also on the hydrogen-oxygen atmosphere. In general, the hydrogen compounds do not play an important role and their reactions with NO and NO_2 can be neglected. There is, however, an



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Fig. 22.- Vertical distribution of the concentration of HNO_3 , NO_2 and NO for two different lower boundary conditions at 15 km and a fixed ratio $n(\text{OH})/n(\text{HO}_2) = 1/9$.



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Fig. 23.- Vertical distribution of the concentration of HNO_3 , NO_2 and NO for two different lower boundary conditions at 15 km and a fixed ratio $n(\text{OH})/n(\text{HO}_2) = 1$.

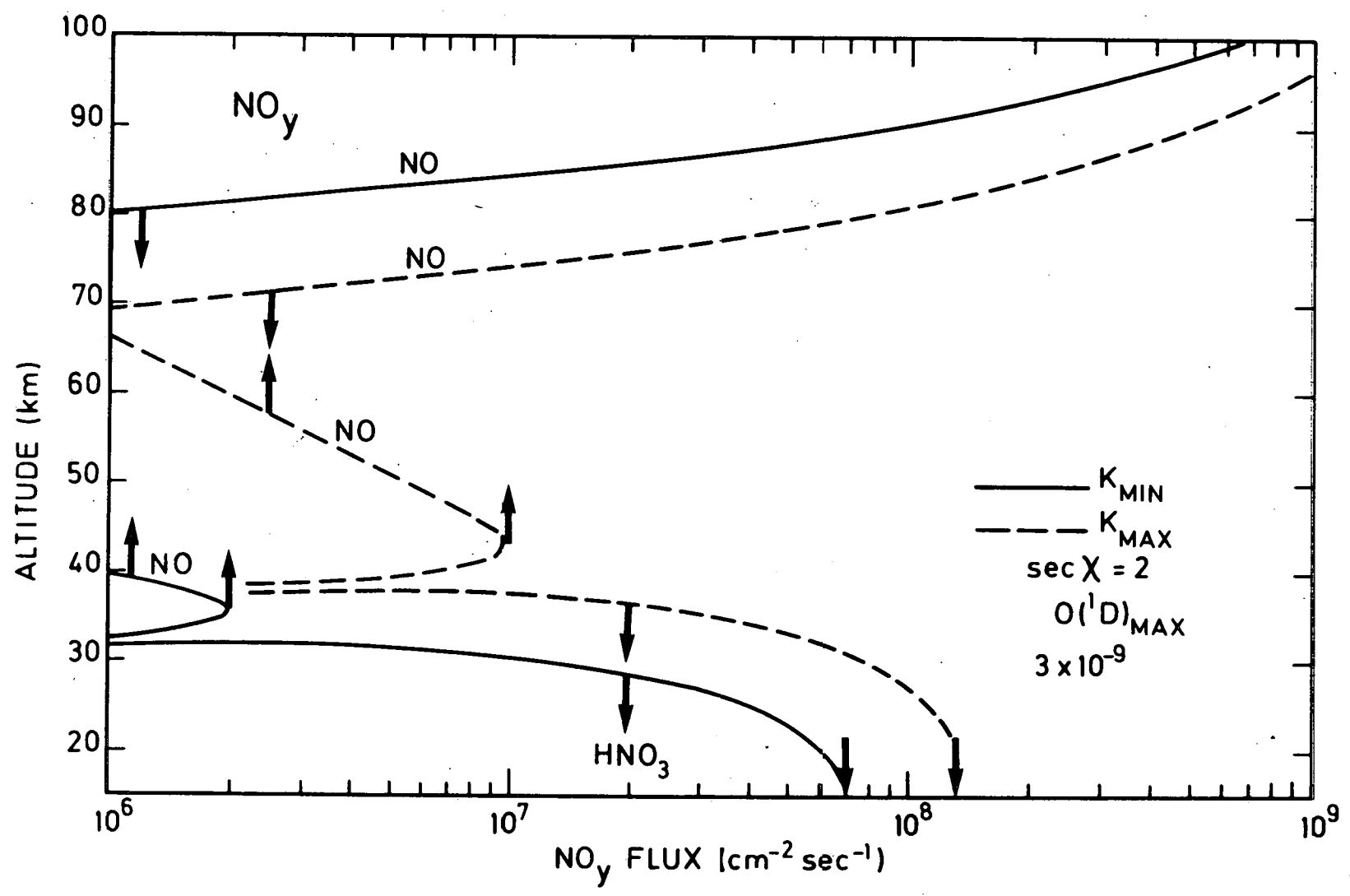


Fig. 24.- Vertical transport of NO and HNO₃ in the mesosphere and stratosphere if NO_y = 3 × 10⁻⁹ at 15 km. Conditions are almost identical if NO_y = 3 × 10⁻⁸.

TABLE 3.- Hydroxyl radicals concentration in the stratosphere (cm^{-3}); ($\sec \chi = 2$)

Altitude	$n(\text{HO}_2)/n(\text{OH}) = 1$	$n(\text{HO}_2)/n(\text{OH}) = 9$
15	5.0×10^5	1.7×10^5
20	1.2×10^6	4.1×10^5
25	2.4×10^6	8.1×10^5
30	4.7×10^6	1.6×10^6
35	7.8×10^6	2.6×10^6
40	1.1×10^7	3.7×10^6
45	1.2×10^7	3.9×10^6
50	1.0×10^7	3.5×10^6

important exception : the formation of nitric acid with OH radicals leads to the introduction in the stratosphere of all aeronomic reactions dealing with the production and loss of hydroxyl and hydroperoxyl radicals.

The absolute value of the NO concentration in the mesosphere depends on transport conditions from the lower thermosphere. However, there is no downward current of nitric oxide at the stratopause level. In the stratosphere, the production of nitric oxide by an oxidation process of nitrous oxide (and the production of nitrogen atoms by cosmic rays) leads to a downward current of nitrogen oxides through the tropopause. The final sink depends on the formation of nitric acid related to a certain destruction of H_2O , CH_4 and H_2 molecules. Nevertheless, the importance of such a sink depends on the values of the horizontal and vertical eddy diffusion coefficients at and above the tropopause. New observational results such as very recent measurements of the mixing ratio of NO_2 by Ackerman and Muller (1972), of HNO_3 by Murcray *et al* (1973), and of NO_2 and HNO_3 by Harries (1972) are still needed, particularly if important quantities of nitric oxide have been injected into the stratosphere after nuclear explosions (Foley and Ruderman, 1972).

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