INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE
3 - Avenue Circulaire
B - 1180 BRUXELLES

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On the behavior of nitrogen oxides in the stratosphere

by

G. BRASSEUR and S.CIESLIK

BELGISCH INSTITUUT VOOR RUIMTE-AERONOMIE
3 - Ringlaan
B - 1180 BRUSSEL

FOREWORD

This paper has been presented at the Symposium on atmospheric ozone held in Arosa, Switzerland, August 21-26, 1972 and at the Climatic Impact Assessment Program (CIAP) meeting sponsored by the U.S. Department of Transportation held at N.B.S. Gaithersburg, Maryland, September 12-13, 1972. It will be published in "Pure and Applied Geophysics".

AVANT-PROPOS

Ce texte a été présenté au Symposium sur l'ozone atmosphérique qui s'est tenu du 21 au 26 Août 1972 à Arosa (Suisse) et à la réunion organisée les 12 et 13 septembre au National Bureau of Standards, Gaithersburg (Maryland) par le Department des Transports des Etats-Unis dans le cadre du Climatic Impact Assessment Program (CIAP). Il sera publié dans "Pure and Applied Geophysics".

VOORWOORD

Deze tekst werd zowel voorgedragen tijdens het "Symposium on atmospheric ozone", 21-26 Augustus, 1972, te Arosa (Zwitserland) als tijdens de CIAP meeting, 12-13 september, 1972 te Gaithersburg, Maryland. Hij zal in "Pure and Applied Geophysics" uitgegeven worden.

VORWORT

Dieser Text wurde zum "Symposium on atmospheric Ozone", 21-26 August, 1972 in Arosa (Schweiz) und zum CIAP meeting, 12-13 September, 1972 in Gaithersburg (Maryland) vorgestellt. Er wird in "Pure and Applied Geophysics" herausgegeben werden.

ON THE BEHAVIOR OF NITROGEN OXIDES IN THE STRATOSPHERE

by

G. BRASSEUR and S. CIESLIK

Abstract

A summary is presented of the relative importance of the principal aeronomic processes determining the vertical distribution of NO-NO_2 in the stratosphere. Formation and destruction of nitric oxide are considered with transport processes for steady state conditions. Estimates of the vertical distribution of NO_x are made for extreme conditions of the eddy diffusion coefficient. It is pointed out that NO is determined by the values which are adopted for its photodissociation coefficient which is related to the absorption of solar radiation in the Schumann-Runge bands of molecular oxygen.

Résumé

L'importance relative des divers phénomènes qui déterminent la distribution verticale des oxydes d'azote dans la stratosphère est examinée. Les mécanismes de formation, de destruction et de transport sont considérés dans un modèle stationnaire. La distribution de NO_x est alors déterminée pour des valeurs extrèmes du coefficient de diffusion turbulente. On constate l'importance jouée par la photodissociation de NO qui dépend de l'absorption de la radiation solaire dans les bandes de Schumann-Runge de l'oxygène moléculaire.

Samenvatting

De vertikale verdeling der stikstofoxyden is afhankelijk van verscheidene verschijnselen. De vorming, de vernietiging en het transport dezer oxyden worden beschouwd in een stationair model. De verdeling van NO_x wordt bepaald voor extreme waarden van de Eddy–diffusie coëfficiënt. Opvallend is de belangrijke rol van de fotodissociatie van NO die afhankelijk is van de absorptie der zonnestraling in het gebied der Schumann-Runge banden van de molekulaire zuurstof.

Zusammenfassung

Die relative Wichtigkeit der verschiedenen Erscheinungen, die die senkrechte Verteilung der Stickstoffoxyden in der Stratosphäre beeinflussen, wird beschrieben. Die Bildung, der Untergang und der Transport werden in einem stationären Model betrachtet. Die NO_x Verteilung wird dann für äussersten Werte des Eddydiffusionskoeffizienten festgestellt. Die NO Photodissoziation, die von der Absorption der Sonnestrahlung in den Sauerstoff Schumann-Runge Banden abhängig ist, spielt eine wichtige Rolle.

Nitric oxide is formed in the lower thermosphere as a result of ionospheric reactions (Norton and Barth [11] ; Strobel *et al* [13]; Nicolet [6]) and occurs in the stratosphere chiefly as a result of a reaction of the electronically excited oxygen atom $O(^1D)$ with nitrous oxide (Nicolet [7]; Nicolet and Vergison [10]; Nicolet and Peetermans [9]; McElroy and McConnell [5]). As far as the dissociation of nitric oxide is concerned, it has been introduced in aeronomic studies by Bates [1]. With an assumed lifetime of the upper states of NO of about 10^{-6} sec, a photodissociation coefficient $J_{NO} = 10^{-7}$ sec^{-1} has been deduced at zero optical depth (Bates [2]; Nicolet [8]) or with a transition probability of about 2×10^{-7} sec^{-1} a coefficient $J_{NO} = 5 \times 10^{-6}$ sec^{-1} (Nicolet [8]). A first investigation by Strobel *et al* [13] has led to $J_{NO} = 4 \times 10^{-6}$ sec^{-1} while a more recent analysis by Strobel [12] gives $J_{NO} \geqslant 10^{-5}$ sec^{-1}.

Since the photodissociation of nitric oxide depends on various predissociation processes occuring in the β, γ, δ and ϵ-bands at $\lambda < 1908$A, we have used the results of Cieslik and Nicolet [4], which are based on the detailed analysis of the absorption depending on the structure of the Schumann-Runge bands of molecular oxygen. Attention will be confined here to the aeronomic conditions of nitrogen oxides in the stratosphere since a general paper by Brasseur and Nicolet [13] covers the subject of related chemical reactions with all references.

The one-dimensional continuity equation which is

$$\frac{\partial n(NO_x)}{\partial t} + \frac{\partial \Phi(NO_x)}{\partial z} + L(NO_x) = P(NO_x) \qquad (1)$$

where Φ is the vertical flux, $L(NO_x)$ and $P(NO_x)$ are respectively the loss and production rates, can be written as follows

$$\frac{\partial n(NO_x)}{\partial t} + \frac{\partial \Phi(NO_x)}{\partial z} + \frac{2\, J_{NO}\, b_6\, n^2(NO_x)}{R[b_6\, n(NO_x) + R\, b_7\, n(O_2)\,]} =$$

$$2\, b_{NO}\, n(O^1D)\, n(N_2O) \quad , \qquad (2)$$

where

$$n(NO_x) = n(NO) + n(NO_2) + n(N)$$

and

$$R = n(NO_x)/n(NO).$$

Two reactions are particularly important. The reaction of atomic nitrogen and nitric oxide

$$N + NO \rightarrow N_2 + O \qquad (3a)$$

with a rate coefficient

$$b_6 = 2 \times 10^{-12}\, T^{1/2}\ cm^3\ sec^{-1} \qquad (3b)$$

and the reaction of atomic nitrogen with molecular oxygen

$$N + O_2 \rightarrow NO + O \qquad (4a)$$

with a rate coefficient

$$b_7 = 5 \times 10^{-13}\, T^{1/2}\, e^{-3500/T}\ cm^3\ sec^{-1} \qquad (4b)$$

are the aeronomic reactions to be considered in the chemosphere.

The ratio $R = n(NO_x)/n(NO)$ is practically equal to $[n(NO_2) + n(NO)]/n(NO)$ in the stratosphere. It can be written

$$R = 1 + \frac{b_4\, n(O_3)}{J_{NO_2} + b_3\, n(O)} \qquad (5)$$

where

$$b_4 = 1 \times 10^{-12}\, e^{-1250/T}\ cm^{-3}\ sec^{-1} \qquad (6a)$$

is the rate coefficient of reaction

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6b)$$

and

$$b_3 = 9 \times 10^{-12}\ cm^{-3}\ sec^{-1} \qquad (7a)$$

is the rate coefficient of reaction

$$O + NO_2 \rightarrow NO + O_2 \qquad (7b)$$

The photodissociation rate of NO_2 is

$$J_{NO_2} = 9.5 \times 10^{-3}\ sec^{-1} \qquad (8)$$

at zero optical depth.

The $n(NO_2)/n(NO)$ ratio is given in figure 1 for a solar zenith angle of 60^0 and for photoequilibrium conditions since the lifetime of a nitrogen dioxide molecule is short in the solar radiation field.

The principal source of odd nitrogen in the stratosphere is the reaction of the electronically excited oxygen atom $O(^1D)$ with nitrous oxide

$$N_2O + O(^1D) \rightarrow 2\ NO \qquad (9a)$$

with a rate coefficient

$$b_{NO} = 10^{-10}\ cm^3\ sec^{-1} \qquad (9b)$$

Additional effects such as the production of nitrogen atoms by the cosmic ray ionization (Nicolet and Peetermans [9]; Warneck [14]) or by a predissociation effect on N_2 have not been considered here. Finally, the vertical flux of NO_x is given by

$$\Phi = -K \left[\frac{\partial n}{\partial z} + \frac{n}{T} \frac{\partial T}{\partial z} + \frac{n}{H} \right] \qquad (10)$$

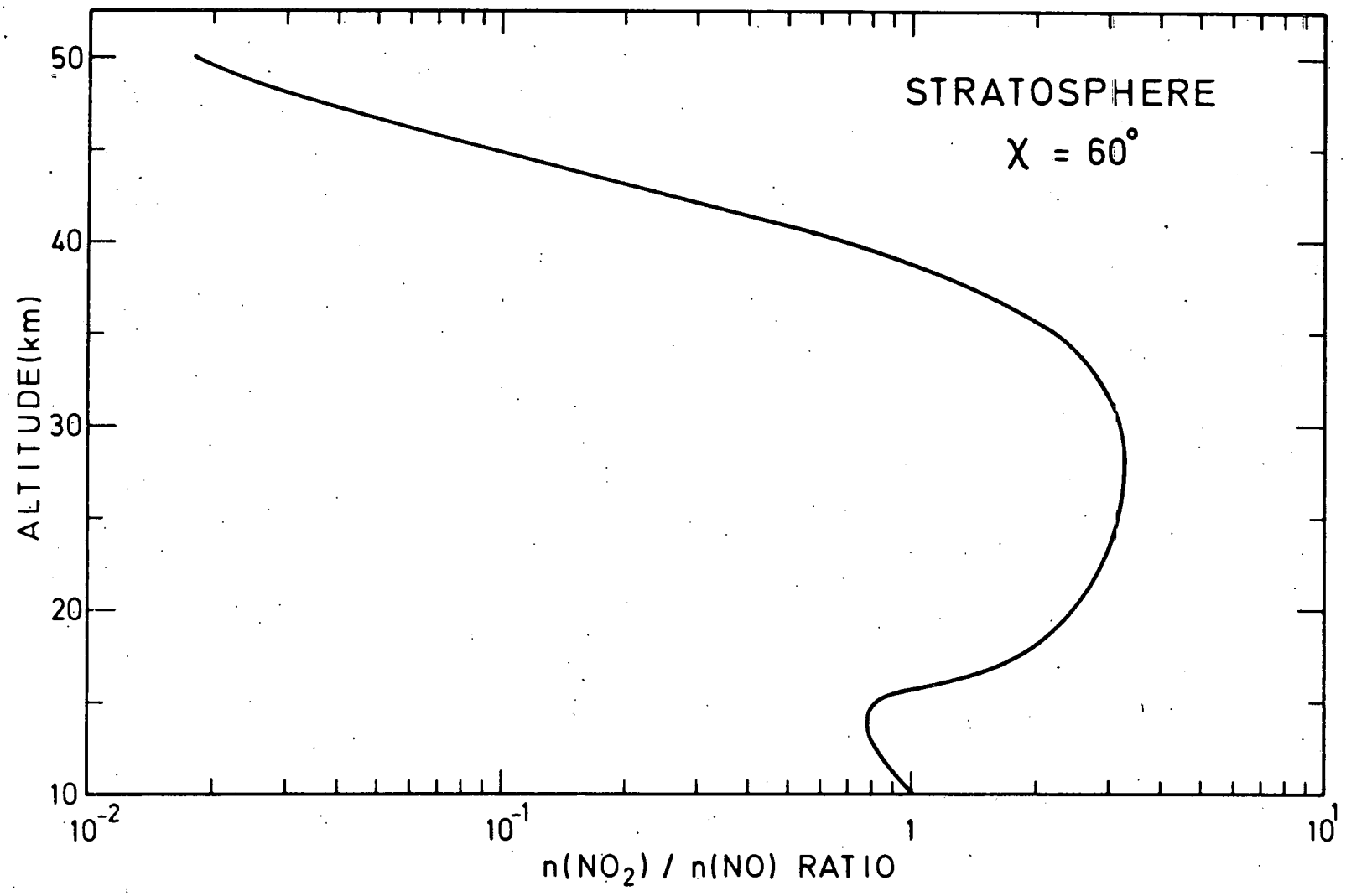

Fig. 1.- Ratio of the NO_2 and NO concentration in the stratosphere calculated for a solar zenith angle of 60^{o}.

where K is the eddy diffusion coefficient. Two analytical profiles called K_{MAX} and K_{MIN} (fig 2) are adopted here as extreme values (see Nicolet and Vergison [10]).

The predissociation which occurs in the δ bands is the most important process of dissociation of NO in the mesosphere and stratosphere (Strobel [12]; Cieslik and Nicolet [4]). Considering that the solar radiation temperature is 4800 ± 50° K in the spectral region λλ 1850 - 1900 A, the photodissociation coefficients due to the absorption in the δ(0-0) and δ(1-0) bands are

$$J_{NO}\,[\delta(0\text{-}0)] = (8.2 \pm 1) \times 10^{-6}\ \text{sec}^{-1} \qquad (11a)$$

and

$$J_{NO}\,[\delta(1\text{-}0)] = (4.5 \pm 1) \times 10^{-6}\ \text{sec}^{-1}\ , \qquad (11b)$$

respectively (Cieslik and Nicolet [4]). An application has been made to the mesosphere and stratosphere with the detailed rotational structure of NO and O_2 and also with the ozone absorption in the stratosphere. The total photodissociation coefficient of NO resulting from this computation is given in figure 3.

The nitrogen oxide distributions have been calculated in the 15-100 km range without considering all possible aeronomic processes but adopting special conditions which are crucially important for the present problem. A nitric oxide concentration of 10^8 cm^{-3} has been taken as upper boundary condition at 100 km with no NO production in the lower thermosphere. On the other hand, three lower boundary values have been adopted at tropopause level (15 km), e.g. 10^{-9}, 3×10^{-9} and 10^{-8} as mixing ratio values for NO_x in order to explore the effect of varying conditions at the tropopause.

When no production process is considered in the lower thermosphere and mesosphere, it is easy to see how important the photodissociation process is. The result is shown in figure 4 where a difference of a factor of not less than 10000 is reached for the nitric oxide concentration at 60 km even with the high eddy diffusion coefficient K_{MAX}.

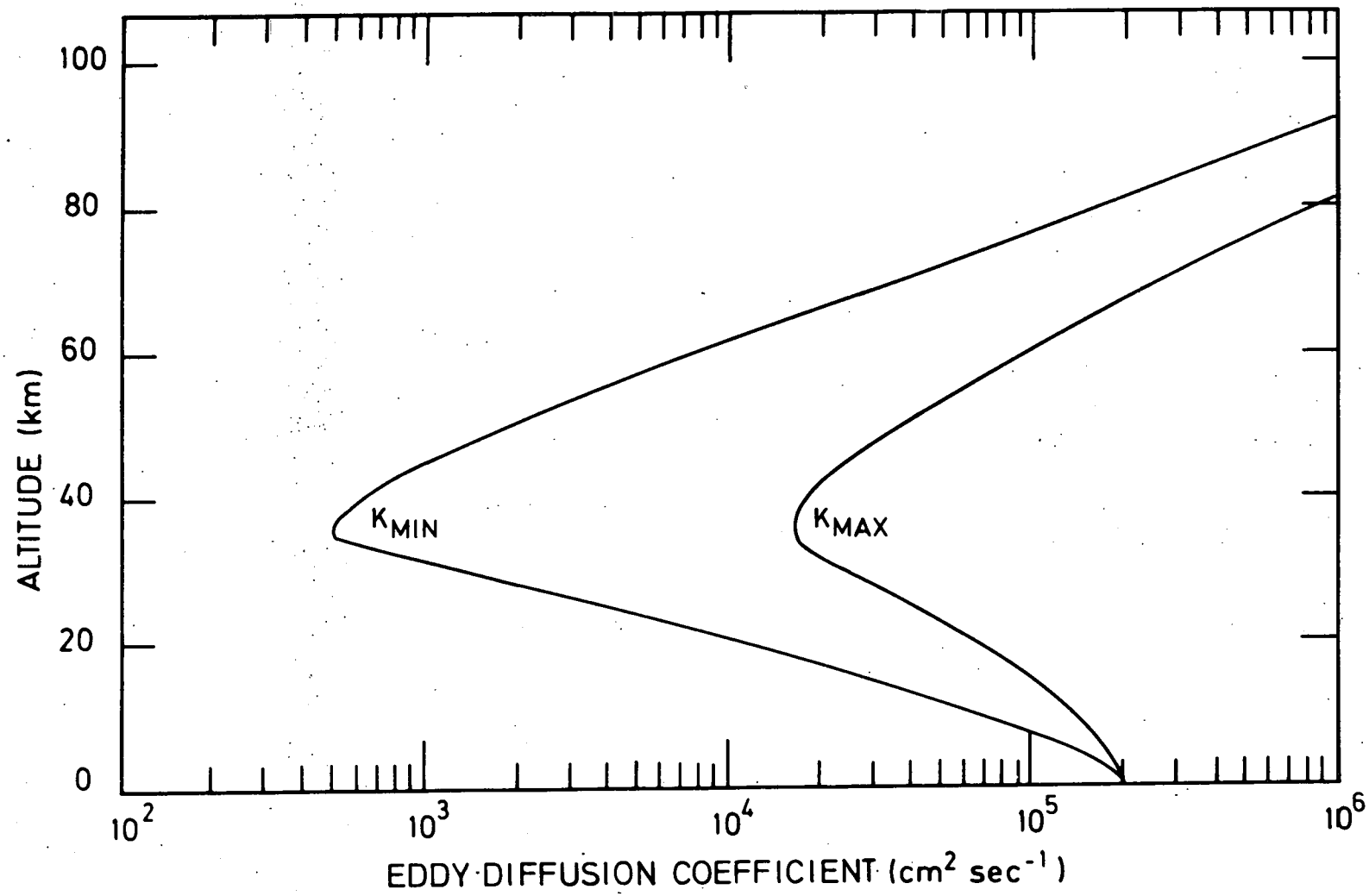

Fig. 2.- Adopted profiles of the eddy diffusion coefficient in the homosphere, K_{MAX} and K_{MIN}.

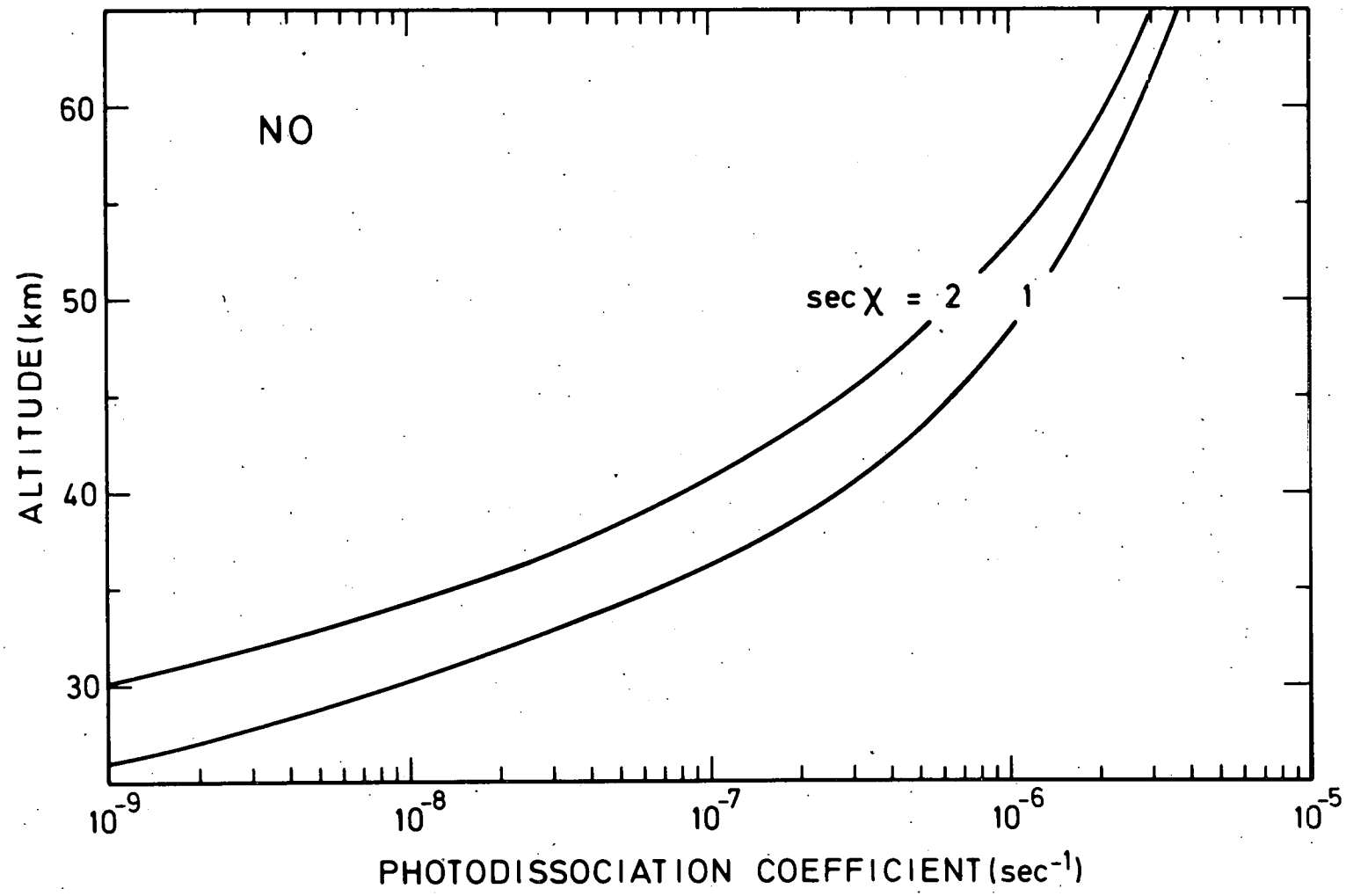

Fig. 3.- Photodissociation rate of NO versus altitude computed for an overhead sun and for a 60^0 zenith angle.

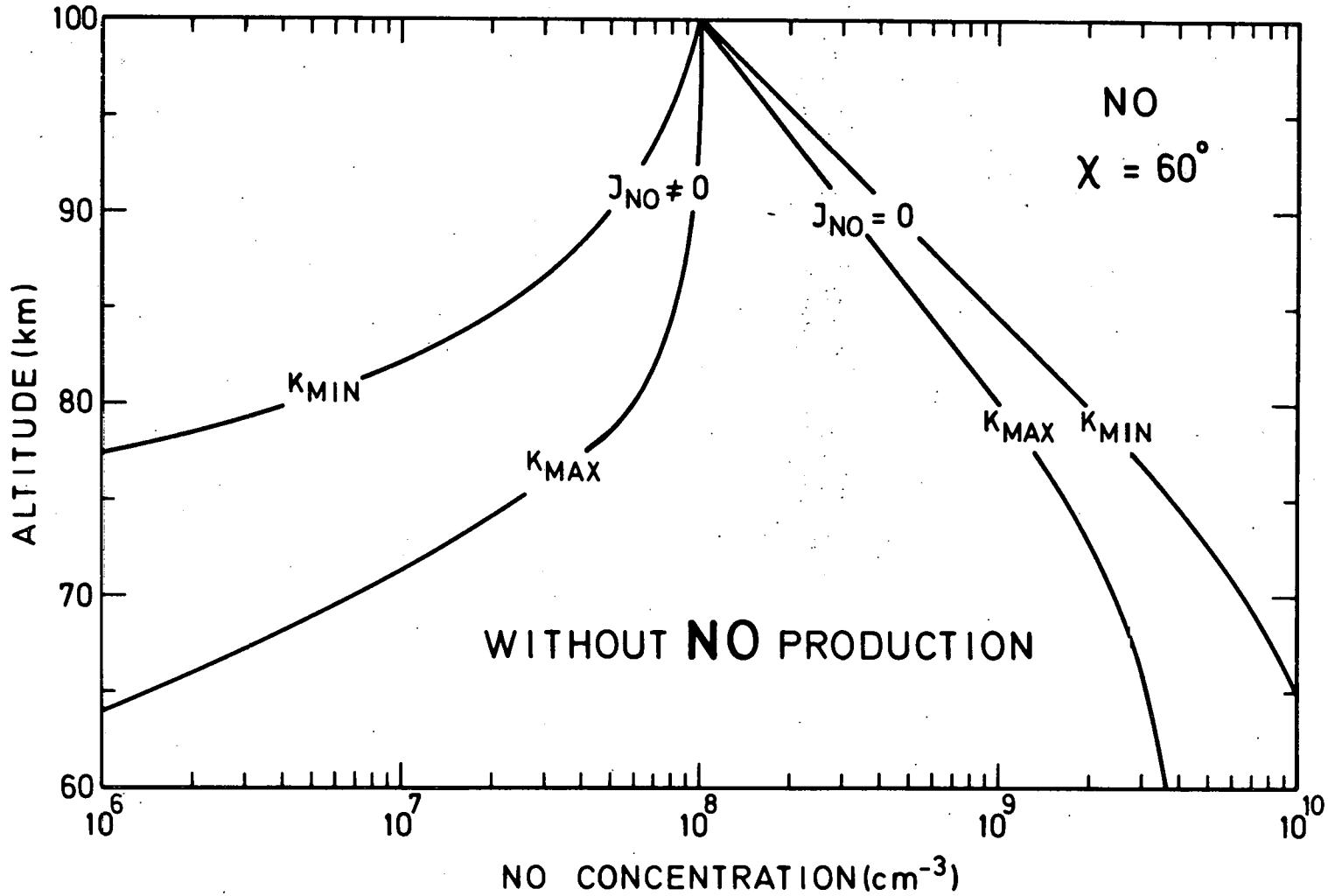

Fig. 4.- Effect of the photodissociation process on the NO distribution in the 60-100 km altitude range computed for two different diffusion coefficients, K_{MAX} and K_{MIN}.

The vertical distribution of NO_x, which is given in Fig. 5 by its volume fractional concentration is related to the vertical production of nitric oxide (see fig. 6) which depends on the values of the eddy diffusion coefficient. The concentration peak is controlled by the production peak of nitric oxide and is not subject to significant influence by the lower boundary conditions. Nevertheless,the absolute values of the nitrogen oxide concentrations in the lower stratosphere are sensitive to the values which are adopted at the tropopause as lower boundary conditions. The two extreme values of the eddy diffusion coefficient, K_{MIN} and K_{MAX}, lead to volume fractional concentrations of 2×10^{-8} and 10^{-8} below and above 35 km, respectively, when the lower boundary condition is taken as $\leqslant 3 \times 10^{-9}$. In addition the NO_x distribution near the stratopause is very sensitive to the value of the eddy diffusion coefficient as illustrated in figure 5.

On the basis of our study it is possible to illustrate the behavior of the nitrogen oxide distribution by the various stratospheric fluxes of NO_x (see fig. 7). At the mesopause level, there is a large downward flux of NO molecules, which are destroyed in the mesosphere.The stratopause is thus much more sheltered from a downward transport of NO molecules than it was generally assumed before. The calculation shows that there is an upward transport in the upper stratosphere. Since no chemical destruction process has been introduced in the lower stratosphere, such as a possible effect of HNO_3, for example, a downward flux of the order of 10^8 cm^{-2} sec^{-1} takes place at the tropopause. A more detailed analysis is required in order to determine the final sinks of nitric oxide.

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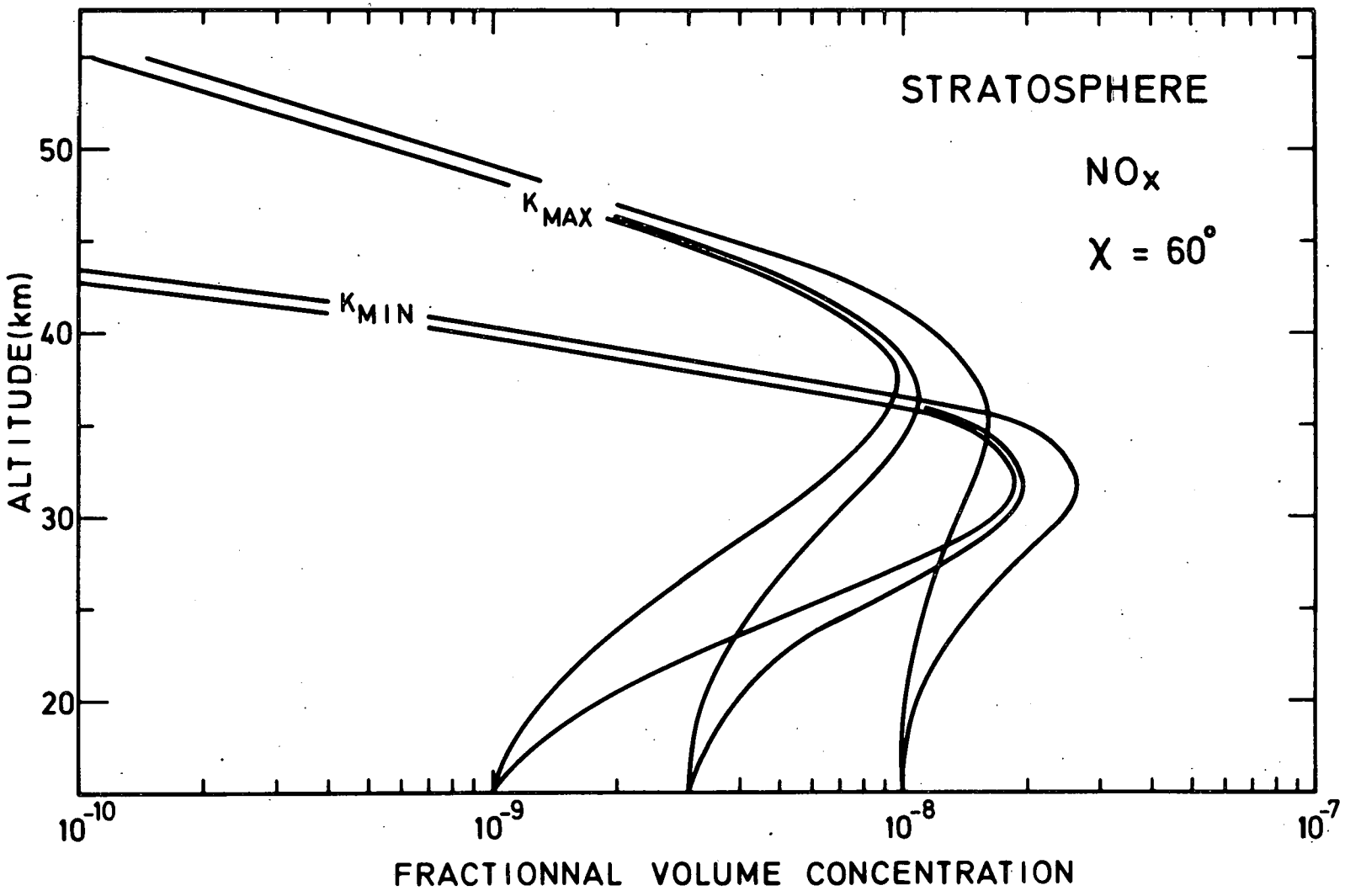

Fig. 5.- Fractional volume concentration of NO_x in the stratosphere for two different eddy diffusion coefficients, K_{MAX} and K_{MIN} and for three lower boundary conditions, 10^{-9}, 3×10^{-9} and 10^{-3}. The zenith angle is 60^0

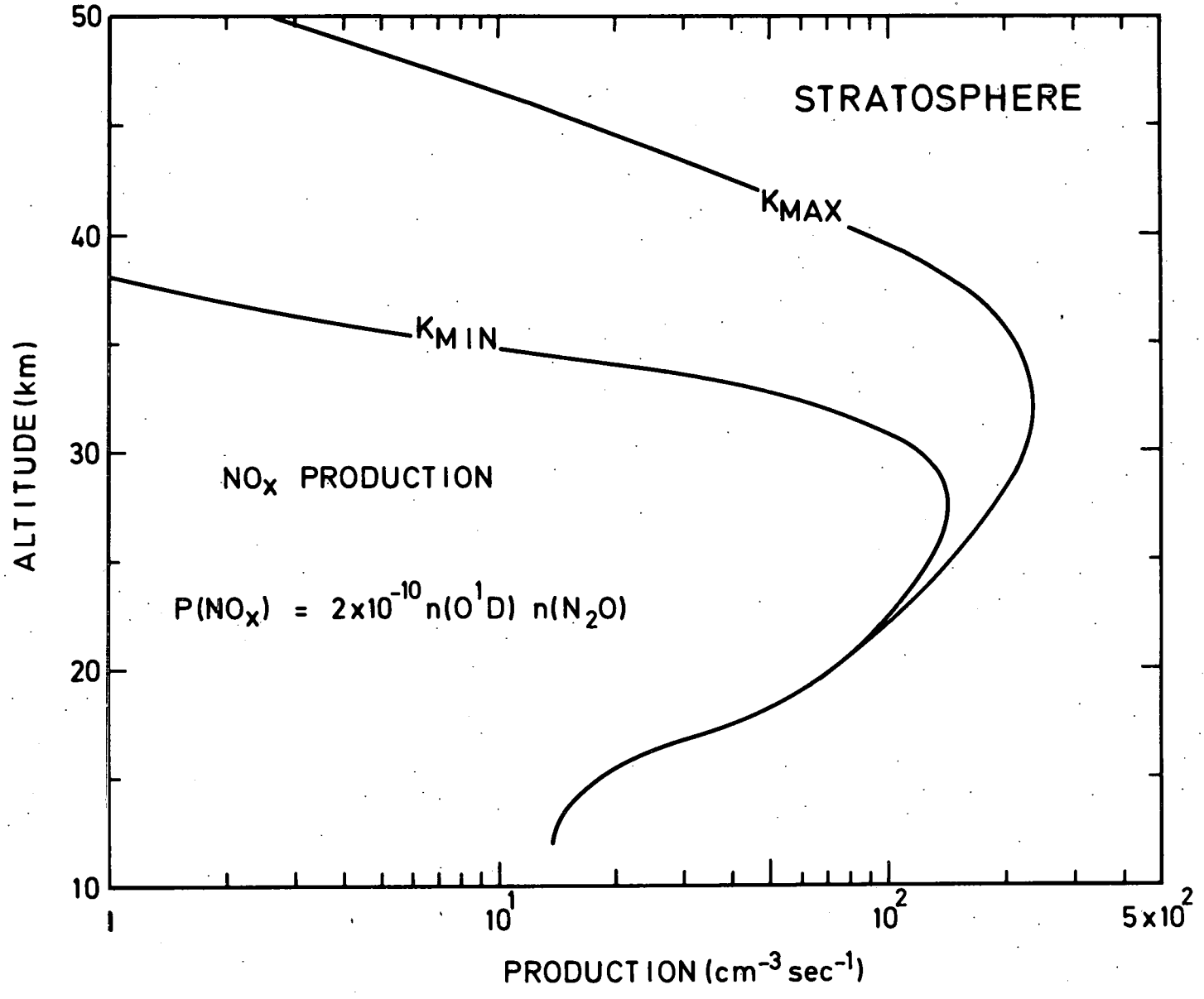

Fig. 6.- Example of nitrogen oxide production in the stratosphere for two different profiles of the eddy diffusion coefficient, K_{MAX} and K_{MIN} and for a sun 30^0 above the horizon.

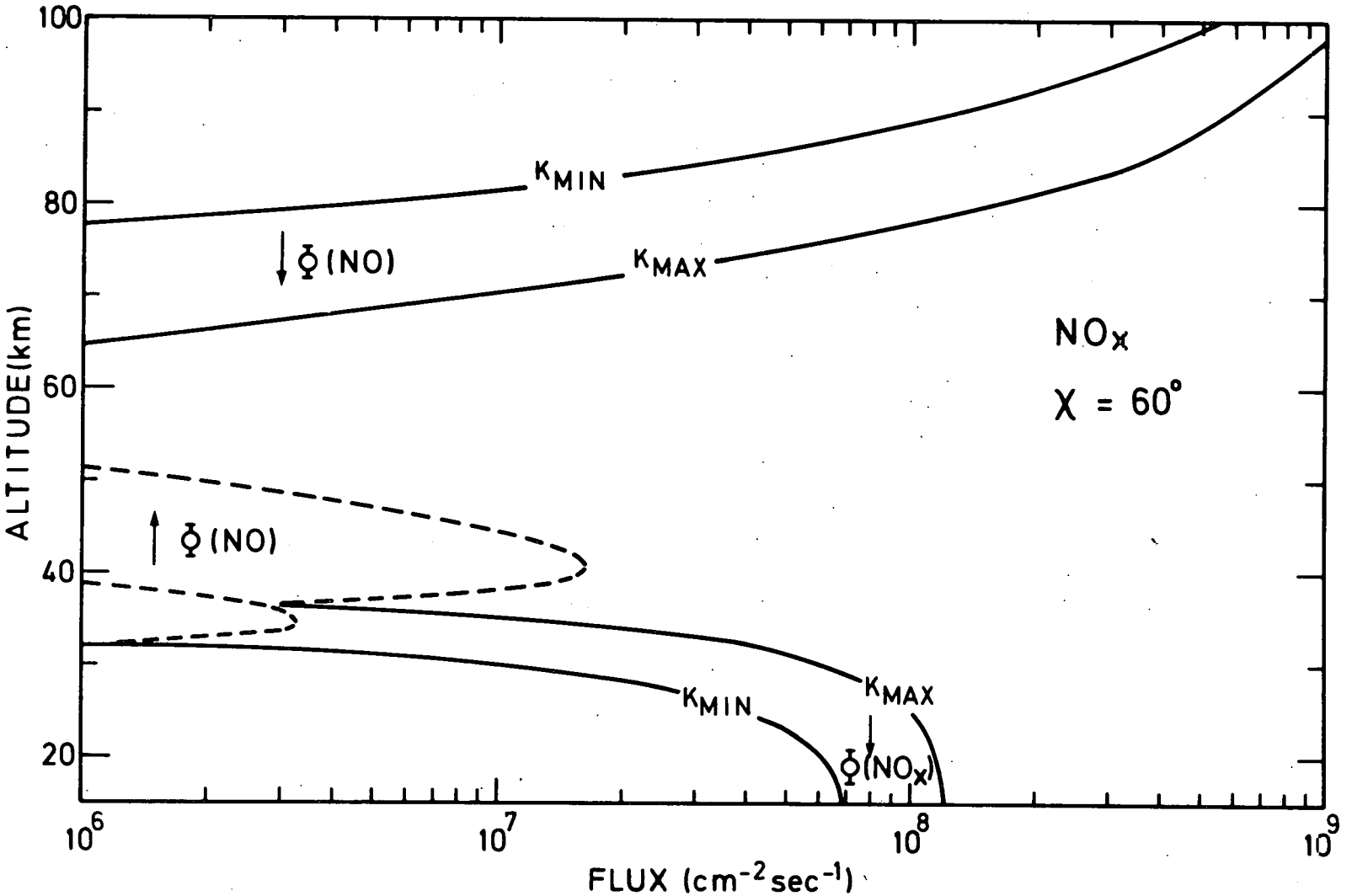

Fig. 7.- NO_x flux in the stratosphere and mesosphere calculated for two eddy diffusion coefficients, K_{MAX} and K_{MIN}. The NO_x mixing ratio was chosen to be 3×10^{-9} at 15 km and the zenith angle is 60^o. The flux is upward in the upper stratosphere and downward elsewhere.

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