

T H E U N I V E R S I T Y O F M I C H I G A N

COLLEGE OF ENGINEERING

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Scientific Report

DISTRIBUTIONS AND LIFETIMES OF N AND NO  
BETWEEN 100 AND 280 Km

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## ABSTRACT

The distribution of N atoms between the altitude range 100 and 280 km has been computed from reactions between constituent particles of the atmosphere and assuming their rate coefficients at laboratory temperature (300°K) to be constant for the whole altitude range. It is also calculated for rate coefficients varying with temperature. It has been found that the latter distribution, which is considerably different from the former, gives a reasonably good profile. Since in many cases, reactions involving loss of N-atoms lead to the production of NO molecules, the altitude distribution of NO molecules is also calculated. The computed N and NO distributions compare favorably with certain rocket experiments and laboratory data. From the loss processes, the lifetimes of N and NO are computed.

## 1. INTRODUCTION

Distributions of ions and neutral particles with altitude have been obtained by rocket-borne mass spectrometers and are computed from reaction rates of upper atmospheric constituents—ions, electrons, and neutral particles. The reaction rates are obtained from laboratory experiments or from theoretical computations. For obtaining the distribution of minor constituents of the atmosphere like N and NO, mass spectrometers may introduce uncertainties due to "wall effect" or dissociation of molecules by accelerated electrons. Again, to determine rates of reactions experimentally for thermal and nearly thermal ions, difficulties are experienced. In theoretical work too, techniques for calculating cross-sections of reactions involving atmospheric particles are yet to be evolved possibly by semiclassical treatments, and methods for calculating cross sections at thermal energies should be devised. Also in many cases, temperature variations of rate coefficients, which may be altered by a factor of several orders by the ambient temperature range at different layers of the upper atmosphere, are not available. However, the altitude distributions of atmospheric ion and neutral particle densities computed with the available collisional data may cross check those obtained by rocket-borne experiments or from rate coefficients determined in the laboratory. Also from the loss processes, the life times of atmospheric particles can be computed.

In this report the altitude distribution of N-atom density between 100 and 280 km is calculated. Since in many cases, reactions involving loss of N atoms are related to the production of NO molecules, its altitude distribution is also calculated. The lifetimes of these particles are also computed.



## 2. COMPUTATION OF N AND NO DISTRIBUTIONS AND LIFETIMES

For computing N-atom distribution, the following scheme has been adopted:

First, to postulate from geophysical observations and laboratory data, conceivable collisional reactions involving N atoms in the atmosphere.

Second, to determine the relative importance of these reactions and for a particular reaction its importance at different layers of the atmosphere, after closely examining the rate coefficients of these reactions as determined by different investigators. A distribution is then obtained by equating the production and loss rates.

The reactions leading to the production of N atoms and their observed rate coefficients obtained by different authors are given in Table 1. The coefficients which are used for the computation are given in the last column. The loss processes and their rate coefficients are given in Table 2.

The reactions which produce NO molecules and those by which they are consumed are given in Tables 3 and 4.

O, O<sub>2</sub>, and N<sub>2</sub> profiles and the temperature distribution of the atmosphere are obtained from CIRA, 1965. For calculating N-atom distribution, a profile of NO is needed which is initially taken for 100-120 km from the Handbook of Geophysics (1960) and for the altitude range 120-280 km from Nawrocki and Papa (1963). After obtaining the NO distribution from reactions given in Tables 3 and 4, the N-atom distribution is recalculated.

The ion distributions (Fig. 1) used for computations are given in Table 5. The electron density is assumed to be the sum of the ion densities.

TABLE 1

## REACTIONS LEADING TO N-ATOM PRODUCTION AND THEIR RATE COEFFICIENTS

Reaction	Observed Rate Coefficient ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )	Rate Coefficient Used For Computation ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )	
		Coefficient at 300°K	Coefficient Varying With Temperature
$\text{N}_2^+ + e \rightarrow \text{N} + \text{N}$	1-2x10 <sup>-7</sup> (Gibbons, 1961) by mass spectrometric technique  3x10 <sup>-7</sup> (Biondi, 1963) for thermal (300°K) electron  7x10 <sup>-7</sup> (Nawrocki, <u>et al.</u> , 1963)	3x10 <sup>-7</sup>	*
$\text{NO}^+ + e \rightarrow \text{N} + \text{O}$	3.5x10 <sup>-7</sup> (Whitten, <u>et al.</u> , 1965) at 300°K  $\approx 10^{-7}$ (Sugden, 1961) at flame temperature	3.5x10 <sup>-7</sup>	Varies as T <sup>-1</sup> from 2x10 <sup>-8</sup> at 2000°K to 6x10 <sup>-7</sup> at 208°K
$\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$	3x10 <sup>-12</sup> (Fehsenfeld, <u>et al.</u> , 1965b) 2x10 <sup>-12</sup> (Danilov, 1966) 1.4x10 <sup>-11</sup> (Dickison, <u>et al.</u> , 1960) 4.7x10 <sup>-12</sup> (Langstroth, <u>et al.</u> , 1962) 2.2x10 <sup>-11</sup> (Galli, <u>et al.</u> , 1963) 6.75x10 <sup>-12</sup> (Talrose, <u>et al.</u> , 1962)	2x10 <sup>-12</sup>	4.2x10 <sup>-12</sup> exp(-470/RT) (E = 0.47 Kcal) Adjusted to 2x10 <sup>-12</sup> at 300°K, E is the activation energy.
$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	2.5x10 <sup>-10</sup> (Ferguson, <u>et al.</u> , 1965)	2.5x10 <sup>-10</sup>	1.0x10 <sup>-7</sup> exp(-3560/RT) (E = 3.56 Kcal) Adjusted to 2.5x10 <sup>-10</sup> at 300°K
$\text{N}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}$	5x10 <sup>-10</sup> (Fehsenfeld, <u>et al.</u> , 1965) 1x10 <sup>-9</sup> (Goldan, <u>et al.</u> , 1966)	1x10 <sup>-9</sup>	1x10 <sup>-9</sup>
$\text{N}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}$	8x10 <sup>-10</sup> (Goldan, <u>et al.</u> , 1966) at 300°K	8x10 <sup>-10</sup>	*
$\text{O}^+ + \text{NO} \rightarrow \text{O}_2^+ + \text{N}$	2.4x10 <sup>-11</sup> (Goldan, <u>et al.</u> , 1966)	2.4x10 <sup>-11</sup>	*
$\text{N}_2 + h\nu \rightarrow \text{N}_2(a^1\pi_g)$	Cross-section, Q = 6x10 <sup>-23</sup> cm <sup>2</sup> (Ditchburn, <u>et al.</u> , 1959)	Q = 1x10 <sup>-21</sup> cm <sup>2</sup>	Q = 1x10 <sup>-21</sup> cm <sup>2</sup>
$\rightarrow \text{N} + \text{N}$	10 <sup>-21</sup> cm <sup>2</sup> (Watanabe, <u>et al.</u> , 1953)		**

\*After computing the N-atom production rates for rate coefficients at 300°K, it was found that for reactions marked (\*), the contributions are small and hence for varying temperature these reactions are not considered.

\*\*Most of the absorption occurs in the (8,0) band at 1226Å (Nicolet, 1960). For this wavelength, the absorption cross section of O<sub>2</sub> is 4x10<sup>-19</sup> cm<sup>2</sup> (Watanabe, 1958) and N(hν)<sub>∞</sub> = 1.5x10<sup>9</sup> photons/cm<sup>2</sup> sec (Gast, et al., 1965).

TABLE 2

## REACTIONS LEADING TO N-ATOM LOSS AND THEIR RATE COEFFICIENTS

Reaction	Observed Rate Coefficient (cm <sup>3</sup> particle <sup>-1</sup> sec <sup>-1</sup> )	Rate Coefficient Used For Computation (cm <sup>3</sup> particle <sup>-1</sup> sec <sup>-1</sup> )	
		Coefficient at 300°K	Coefficient Varying With Temperature
$O_2^+ + N \rightarrow NO^+ + O$	$2 \times 10^{-10}$ at 300°K (Goldan, <u>et al.</u> , 1966)	$2 \times 10^{-10}$	$2.9 \times 10^{-9} \exp(-1590/RT)$ (E = 1.59 Kcal) Adjusted to $2 \times 10^{-10}$ at 300°K
$N_2^+ + N \rightarrow N_2 + N^+$	$< 10^{-11}$	$1 \times 10^{-11}$	$4 \times 10^{-9} \exp(-3560/RT)$ (E = 3.56 Kcal) Adjusted to $1 \times 10^{-11}$ at 300°K
$N + N + M \rightarrow N_2 + M$	$7.4 \times 10^{-33}$ cm <sup>6</sup> particle <sup>-2</sup> sec <sup>-1</sup> (200-450°K) (Herron, <u>et al.</u> , 1958)  $1.7 \times 10^{-32}$ at 300°K (Harteck, <u>et al.</u> , 1958)	$7.4 \times 10^{-33}$ cm <sup>6</sup> particle <sup>-2</sup> sec <sup>-1</sup>	*,**
$N + O + M \rightarrow NO + M$	$1.5 \times 10^{-32}$ cm <sup>6</sup> particle <sup>-2</sup> sec <sup>-1</sup> (at 300°K) (Kaplan, <u>et al.</u> , 1958)  $5 \times 10^{-33}$ (Byron, 1959)	$5 \times 10^{-33}$ cm <sup>6</sup> particle <sup>-2</sup> sec <sup>-1</sup>	
$N + N \rightarrow N_2 + hv$	$\leq 10^{-14}$ (Nawrocki, <u>et al.</u> , 1963)	$1 \times 10^{-17}$	$1.7 \times 10^{-16} T^{-1/2}$ Adjusted to $1 \times 10^{-17}$ at 300°K
$N + O \rightarrow NO + hv$	$\leq 10^{-14}$ (Nawrocki, <u>et al.</u> , 1963)  $1 \times 10^{-17}$ (Young, <u>et al.</u> , 1963)	$1 \times 10^{-17}$	$1.7 \times 10^{-16} T^{-1/2}$ Adjusted to $1 \times 10^{-17}$ at 300°K
$N + O_2 \rightarrow NO + O$	$3.3 \times 10^{-12} \exp(-3100/T)$ (Kistiakowsky, 1957) $1 \times 10^{-16}$ at 300°K (Harteck, <u>et al.</u> , 1957)	$1 \times 10^{-16}$	$3.3 \times 10^{-12} \exp(-3100/T)$
$N + NO \rightarrow N_2 + O$	$8 \times 10^{-11}$ at 300°K (Kistiakowsky, 1958)  $1-3 \times 10^{-13}$ at 300°K (Harteck, <u>et al.</u> , 1957)  $1.5 \times 10^{-12} T^{1/2}$ (Nicolet, 1965a)	$2.6 \times 10^{-11}$	$1.5 \times 10^{-12} T^{1/2}$

\*After computing the N-atom production rates for rate coefficients at 300°K, it was found that for reactions marked (\*), the contributions are small and hence for varying temperature these reactions are not considered.

\*\*n(M) is assumed to be equal to n(O<sub>2</sub>) + 0.6n(N<sub>2</sub>) (Young, et al., 1962).

TABLE 3

## REACTIONS LEADING TO NO PRODUCTION AND THEIR RATE COEFFICIENTS

Reaction	Observed Rate Coefficient ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )	Rate Coefficient Used For Computation ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )
$\text{N}+\text{O} \rightarrow \text{NO}+\text{h}\nu$	$1 \times 10^{-17}$ (Young, et al., 1963)	$1.7 \times 10^{-16} \text{ T}^{-1/2}$ Adjusted to $1 \times 10^{-17}$ at $300^\circ\text{K}$
$\text{N}+\text{O}+\text{M} \rightarrow \text{NO}+\text{M}$	$1.5 \times 10^{-32} \text{ cm}^6 \text{ particle}^{-2} \text{ sec}^{-1}$ at $300^\circ\text{K}$ (Kaplan, et al., 1958)	**
$\text{N}+\text{O}_2 \rightarrow \text{NO}+\text{O}$	$5 \times 10^{-33}$ (Byron, 1959)	
	$2 \times 10^{-13} \text{ T}^{-1/2} \exp(-300/\text{T})$ (Micolet, 1965a)	
	$1 \times 10^{-16}$ at $300^\circ\text{K}$ (Hartecck, et al., 1957)	$3.3 \times 10^{-12} \exp(-3100/\text{T})$
	$3.3 \times 10^{-12} \exp(-3100/\text{T})$ (Kistiakowsky, et al., 1957)	
$\text{O}+\text{NO}_2 \rightarrow \text{NO}+\text{O}_2$	$3.5 \times 10^{-12}$ at $300^\circ\text{K}$ (Ford, et al., 1957b)	*
$2\text{NO}$	$5 \times 10^{-14}$	
$\text{N}+\text{NO}_2 \rightarrow \text{N}_2\text{O}+\text{O}$	$3 \times 10^{-14}$ at $300^\circ\text{K}$ (Hartecck, et al., 1957)	*
$\text{N}_2+\text{O}_2$	$2 \times 10^{-14}$	
$\text{N}_2^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{NO}$	$1 \times 10^{-13}$ , $E = 7 \text{ Kcal}$ (Whitten, et al., 1965) $4 \times 10^{-13}$ by afterglow technique (Fehsenfeld, et al., 1965a) $< 10^{-14}$ (Hartecck, et al., 1961) $\leq 2.1 \times 10^{-13}$ (Galli, et al., 1963)	**
$\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$	$7.5 \times 10^{-11} \text{ T}^{1/2} \exp(-6000/\text{RT})$ (Micolet, 1965b) $< 2 \times 10^{-13}$ (Galli, et al., 1963)	$7.5 \times 10^{-11} \text{ T}^{1/2} \exp(-6000/\text{RT})$

\* $\text{N}_2\text{O}$  and  $\text{NO}_2$  do not affect appreciably the  $\text{NO}$  concentration and hence reactions involving these molecules are not considered.

\*\*These reactions are not considered as their contributions for  $300^\circ\text{K}$  or for varying temperatures are small.

TABLE 4

## REACTIONS LEADING TO NO LOSS AND THEIR RATE COEFFICIENTS

Reaction	Observed Rate Coefficient ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )	Rate Coefficient Used for Computation ( $\text{cm}^3 \text{ particle}^{-1} \text{ sec}^{-1}$ )
$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$1.5 \times 10^{-12} \text{ T}^{1/2}$ (Nicolet, 1965a)	$1.5 \times 10^{-12} \text{ T}^{1/2}$
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$8 \times 10^{-11}$ at $300^\circ\text{K}$ (Kistiakowski, 1958)	
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$5 \times 10^{-14}$ at $300^\circ\text{K}$ (Ford, et al., 1957a) $1.7 \times 10^{-14}$ at $300^\circ\text{K}$ (Johnston, et al., 1951)	*
$\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$5.2 \times 10^{-32} \text{ cm}^6 \text{ particle}^{-2} \text{ sec}^{-1}$ at $300^\circ\text{K}$ (Ford, et al., 1957b)	*
$\text{O} + \text{NO} \rightarrow \text{NO}_2 + \text{hv}$	$2.5 \times 10^{-17}$ for average quanta of 5500A (Kaufman, 1958)	$4.3 \times 10^{-16} \text{ T}^{-1/2}$ *
$\text{NO} + \text{hv} (1216\text{A}) \rightarrow \text{NO}^+ + \text{e}$	Cross-section $Q = 2 \times 10^{-18} \text{ cm}^2$ (Matanabe, 1959)	$Q = 2 \times 10^{-18} \text{ cm}^2$
$\text{NO} + \text{hv} (1900\text{A}) \rightarrow \text{N} + \text{O}$	$Q = 2 \times 10^{-19} \text{ cm}^2$	$Q = 2 \times 10^{-19} \text{ cm}^2$
$\text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}$ $\rightarrow \text{O}_2^+ + \text{N}$	$2.4 \times 10^{-11}$ at $300^\circ\text{K}$ (Goldan, et al., 1966)	$4.6 \times 10^{-8} \exp(-4500/\text{RT})$ ( $E = 4.5 \text{ Kcal}$ ) Adjusted to $2.4 \times 10^{-11}$ at $300^\circ\text{K}$
$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	$8 \times 10^{-10}$ at $300^\circ\text{K}$ (Goldan, et al., 1966)	$1.5 \times 10^{-6} \exp(-4500/\text{RT})$ ( $E = 4.5 \text{ Kcal}$ ) Adjusted to $8 \times 10^{-10}$ at $300^\circ\text{K}$

\*These reactions are not considered as their contributions for  $300^\circ\text{K}$  or for varying temperatures are small.



TABLE 5

## ALTITUDE DISTRIBUTIONS OF IONS

Ion	Altitude Range (km)
$O^+$	100-200 (Whitten, <u>et al.</u> , 1964) 200-250 (Johnson, 1966) 260-280*
$O_2^+$	100-240 (Whitten, <u>et al.</u> , 1964) 240-280**
$N_2^+$	100-220 (Whitten, <u>et al.</u> , 1964) 220-280**
$N^+$	130 (Ghosh, <u>et al.</u> , 1964) 140-220 (Johnson, 1966) 220-280**
$NO^+$	100-200 (Whitten, <u>et al.</u> , 1964) 200-240 (Johnson, 1966) 240-280**

\*For the altitude range 260-280 km,  $O^+$  and electron distributions (Cormier, 1965) are assumed same.

\*\*Extrapolated to follow the trend given in Fig. 3 (Ghosh, et al., 1964).

Assuming rate coefficients for various reactions at 300°K given in column 3 of Tables 1 and 2, the production and loss rates of N for the altitude range 100-280 km are computed and are given in Figs. 2-4.\* The corresponding rates for rate coefficients varying with temperature given in the last columns of the above tables, are computed and are illustrated in Figs. 4-6. A comparison of Figs. 2-4 with Figs. 4-6 shows that the production and loss rates of N atoms are significantly altered if the temperature variation of rate coefficients, which may sometimes be altered by several orders in the above altitude range, are considered.

\*For calculating N-atom production by predissociation using the formula

$$2n(\text{N}_2)_z Q N(h\nu)_z$$

(the factor 2 accounts for the production of two neutral atoms), it has been assumed that above altitude  $z$ , photons are absorbed mainly by  $\text{O}_2$ , so that the photon flux of frequency  $\nu$  at an altitude  $z$  for overhead sun is given by

$$N(h\nu)_z = N(h\nu)_\infty \exp(-\tau)$$

where

$$\tau(z) = \int_z^\infty \sigma_{\text{O}_2} n(\text{O}_2)_{z'} \exp(-z'/H_{\text{O}_2,z}) dz'$$

$N(h\nu)_\infty$  = number of photons of frequency  $\nu$  outside the earth's atmosphere =  $1.5 \times 10^9$  photons/cm<sup>2</sup> sec for 1226A (Gast, et al., 1965)

$H_{\text{O}_2,z}$  = scale height of  $\text{O}_2$  molecules at an altitude  $z$

$Q$  = cross-section for absorption of 1226A by  $\text{N}_2$  molecules =  $1 \times 10^{-21}$  cm<sup>2</sup>

$\sigma_{\text{O}_2}$  = cross-section for absorption of 1226A by  $\text{O}_2$  molecules =  $4 \times 10^{-19}$  cm<sup>2</sup> (Watanabe, 1958)

$n(\text{N}_2)_z$  = concentration of  $\text{N}_2$  molecules at altitude  $z$

$n(\text{O}_2)_z$  = concentration of  $\text{O}_2$  molecules at altitude  $z$ .

Again, for calculating the production and loss rates from neutral-neutral or ion-neutral particle reactions, the usual formula, namely, the rate is equal to the product of rate coefficient and concentrations of the reacting particles, is used.

The calculated rates of production and loss of NO molecules for rate coefficients varying with temperature are shown in Figs. 7 and 8.

After calculating the loss rates of N atoms, it is found that the lifetime of N atoms for the altitude range 100-280 km varies between  $5.7 \times 10^4$  and  $1.3 \times 10^3$  sec (Table 6 and Figs. 4 and 6).

The N-atom distribution is calculated by equating the production and loss rates (Fig. 9). In a similar manner for 100-280 km the distribution of NO (Fig. 9), for which the lifetime varies between  $3.6 \times 10^2$  and 58 sec (Table 6 and Fig. 8), is calculated.

TABLE 6  
LIFETIMES OF N AND NO

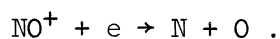
Altitude (km)	Lifetime of NO (sec)	Lifetime of N (sec)
100	$3.6 \times 10^2$	$5.7 \times 10^4$
110	$2.9 \times 10^2$	$1.9 \times 10^4$
120	$2.5 \times 10^2$	$5.7 \times 10^3$
130	$1.8 \times 10^2$	$2.1 \times 10^3$
140	$1.2 \times 10^2$	$1.3 \times 10^3$
150	$9.1 \times 10^1$	$1.6 \times 10^3$
160	$7.4 \times 10^1$	$2.2 \times 10^3$
170	$6.7 \times 10^1$	$2.7 \times 10^3$
180	$6.3 \times 10^1$	$3.3 \times 10^3$
190	$5.9 \times 10^1$	$4.0 \times 10^3$
200	$5.8 \times 10^1$	$4.8 \times 10^3$
220	$7.3 \times 10^1$	$7.1 \times 10^3$
240	$1.0 \times 10^2$	$1.0 \times 10^4$
250	$1.1 \times 10^2$	$1.7 \times 10^4$
260	$1.2 \times 10^2$	$2.2 \times 10^4$
280	$1.0 \times 10^2$	$3.9 \times 10^4$

### 3. CONCLUSIONS

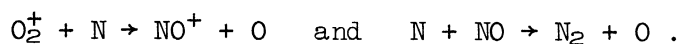
1. After analyzing various reactions leading to the production and loss of N and NO, it may be concluded that the predissociation of N<sub>2</sub> molecules does not contribute significantly to the production of N atoms. In the higher region, they are produced mainly by the ion-atom interchange reaction



and in the lower region, jointly with the reaction



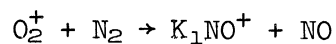
N atoms are lost by the following reactions



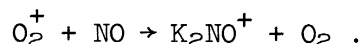
The computed N distribution shows that the first reaction is important at the upper and the latter at the lower region.

The accuracy of calculated N and NO distributions is limited mainly by the values of rate coefficients of reactions (the coefficients are now believed to be accurate by orders but not by factors) and their temperature variations.

For the major portion of 100-280 km altitude range, the NO production and loss rates are given, respectively, by



and



At equilibrium

$$k_1 n(O_2^+) n(N_2) = k_2 n(O_2^+) n(NO)$$

$$n(NO) = \frac{k_1}{k_2} n(N_2)$$

Therefore  $n(NO)$  distribution follows  $(N_2)$  profile and is independent of N-atom distribution (see Fig. 9).

2. From the rocket-borne mass spectrometric measurements of neutral constituents in the altitude range 100-200 km, Hedin and Nier (1965) concluded that the concentration of N atoms is about 1% of  $N_2$ . Again the mass spectrometric data obtained by Schaefer constantly show a small increase of N over laboratory calibrations. Also, from the analysis of peak heights for N and  $N_2$  between 100 and 200 km, it is found that atomic nitrogen does not occur more than 3% of  $N_2$  (Mirtov, 1964). The computed N distribution shows that at the upper region of the above altitude range N is about 1-3% of  $N_2$ . In the lower region the percentage is much smaller. Therefore, for accurate determination of N-atom concentration by a rocket-borne mass spectrometer, it should be measured above 200 km where its concentration becomes relatively larger.

3. By observing absorption of solar radiations in a rocket-borne spectrograph with pointing control, Jursa, et al. (1959), obtained the upper limit of NO molecules as  $10^{15}$  molecules  $cm^{-2}$  above the altitude range 63-87 km. Again, Barth (1964) obtained a NO column density of  $1.5 \times 10^{13}$  molecules  $cm^{-2}$  above 125 km. This agrees with the value obtained from the computed curve which gives about  $3 \times 10^{13}$  molecules  $cm^{-2}$  column $^{-1}$  above this altitude.

4. NI(5200A,  $^2D-^4S$ ) line is observed in twilight and night airglows and appears with an intensity less than 5R at night and 1OR at twilight (Silverman, et al., 1965). Assuming that this line is emitted at 90-100 km and that the lifetime of the  $N(^2D)$  atom is about 26 hours (Hunten, et al., 1966), the concentration of N atoms at twilight can be obtained from the rate of production and quenching of the  $N(^2D)$  atoms, namely

$$n(N)Bn(h\nu) = n(N^2D)[A+n(M)\gamma]$$

where

- $n(N)$  = concentration of normal N atoms
- $n(M)$  = concentration of third body =  $n(O_2) + 0.6n(N_2)$
- $n(N^2D)$  = concentration of  $N(^2D)$  atoms
- A, B = A and B coefficients for  $^2D-^4S$  transition of N atoms
- $n(h\nu)$  = solar photon flux density for 5200A
- $\gamma$  = rate coefficient for collisional deactivation of  $N(^2D)$  atoms

Therefore, the emission rate of 5200A line is given by

$$r = n(N^2D)A = \frac{n(N)Bn(h\nu)}{A + n(M)\gamma} A$$

Substituting B in terms of A and  $n(h\nu)$  from Planck's formula,\* we obtain

$$n(N) = \frac{r(A+n(M)\gamma)}{A^2 D} \exp(h\nu/kT) ,$$

where

$$D = \text{dilution factor} = 5.41 \times 10^{-6}, \text{ and}$$

$$k = \text{Boltzmann constant.}$$

No precise information regarding the quenching cross-section involving metastable atoms is available. According to Laidler (1954) the coefficient of quenching reactions involving nonmetastable atoms is of the order of  $10^{-12}$  cm<sup>3</sup>/particle sec. The coefficient for the metastable N(<sup>2</sup>D) atoms by N<sub>2</sub> and O<sub>2</sub> is assumed to be one order smaller than the above value, that is,  $\gamma = 10^{-13}$  cm<sup>3</sup>/particle sec. Assuming the sun's temperature T = 6000°K and the mean altitude of emission of 5200Å line at twilight to be 90 km, we obtain  $n(N) = 3 \times 10^7$  cm<sup>-3</sup>. The computed N-atom distribution shows that at 100 km the concentration is  $1 \times 10^8$  cm<sup>-3</sup>.

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\*In the visible region the number of photons calculated from Planck's black-body formula for T = 6000°K agrees with the observed value.



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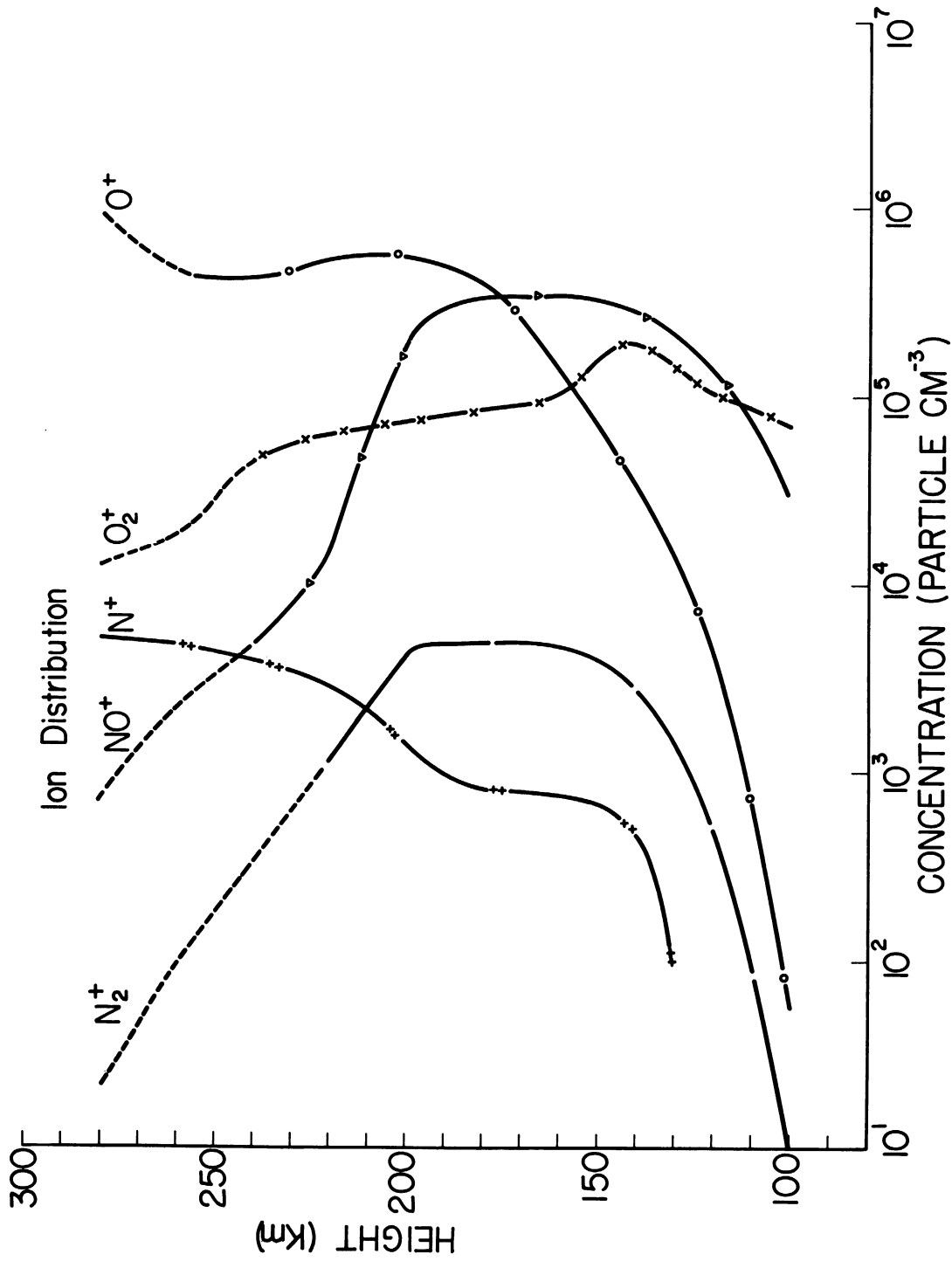


Fig. 1. Variations of assumed ion densities with altitude. Solid curves are obtained from rocket-borne experiments. The broken curves are extrapolated (see Table 5).

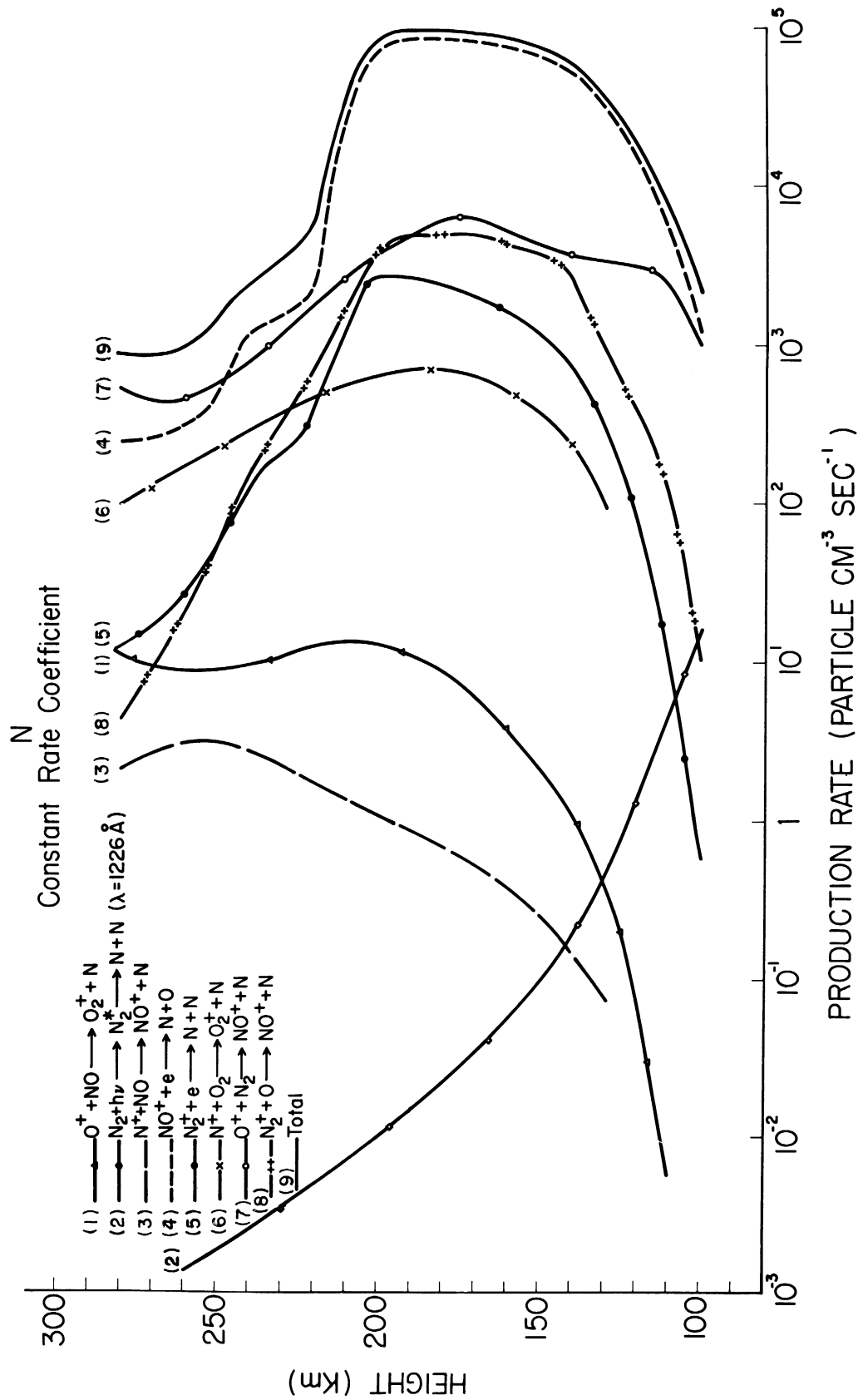


Fig. 2. Production rates of N atoms by various reactions for rate coefficients at laboratory temperature (300°K) assumed constant for the whole altitude range.

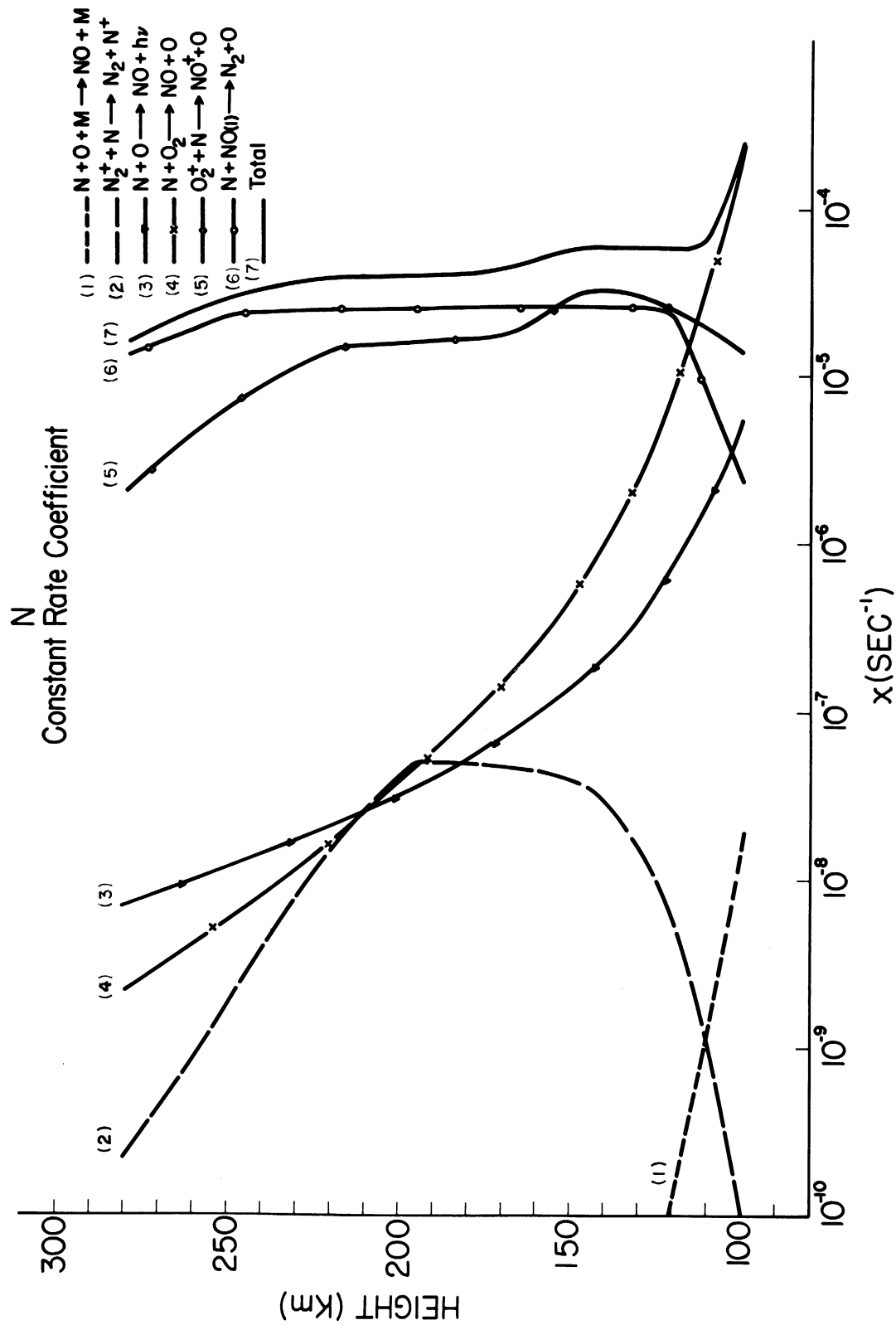


Fig. 3. Variation of  $x$  with altitude for rate coefficients at laboratory temperature (300°K) assumed constant for the whole altitude range. To obtain loss rate of N atoms, multiply  $x$  by  $[N]$ .

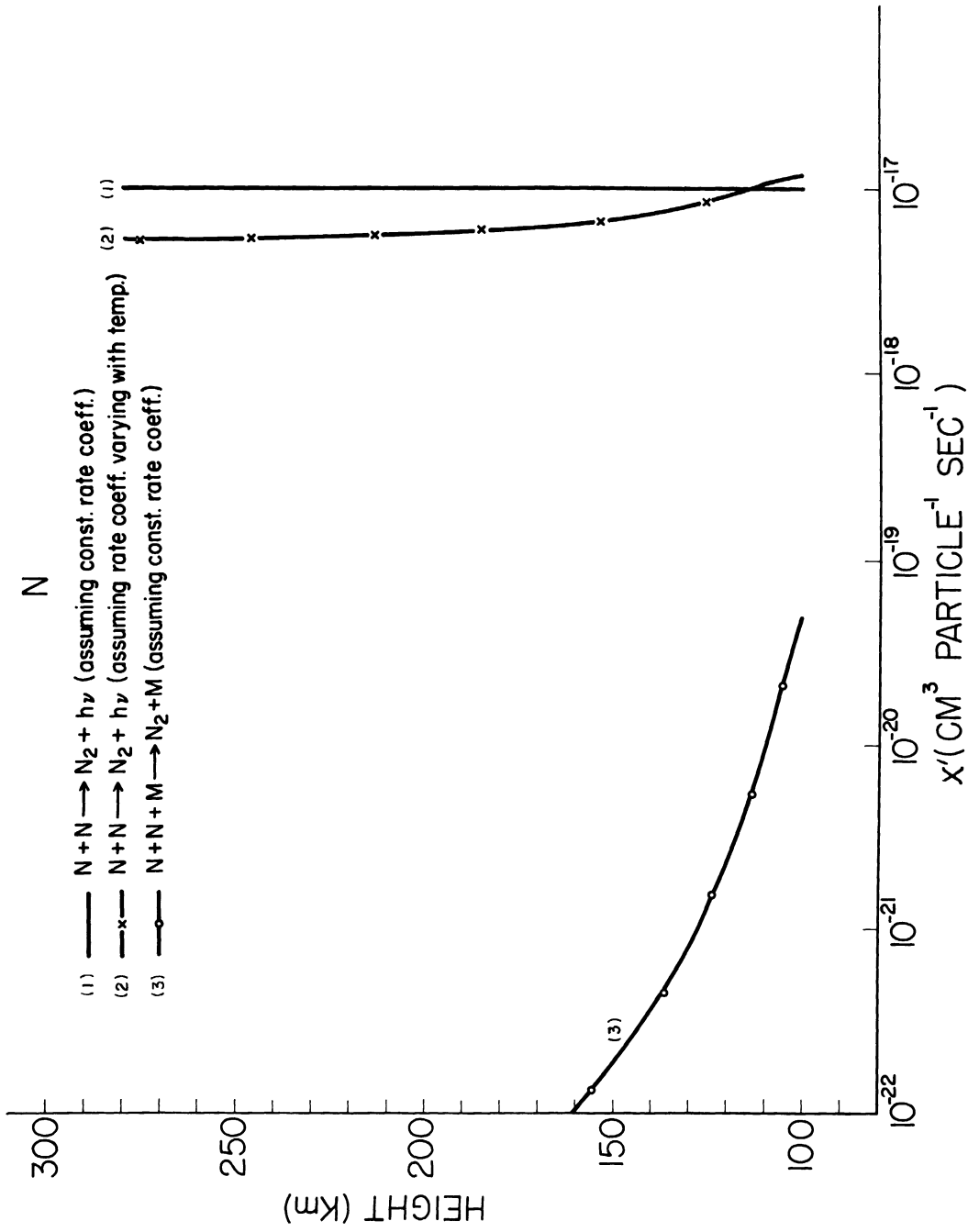


Fig. 4. Variation of  $x'$  with altitude for reactions involving 2 nitrogen atoms. To obtain loss rate multiply  $x'$  by  $[N]^2$ . Loss rates by three-body reactions are very small compared with those for two-body reactions.

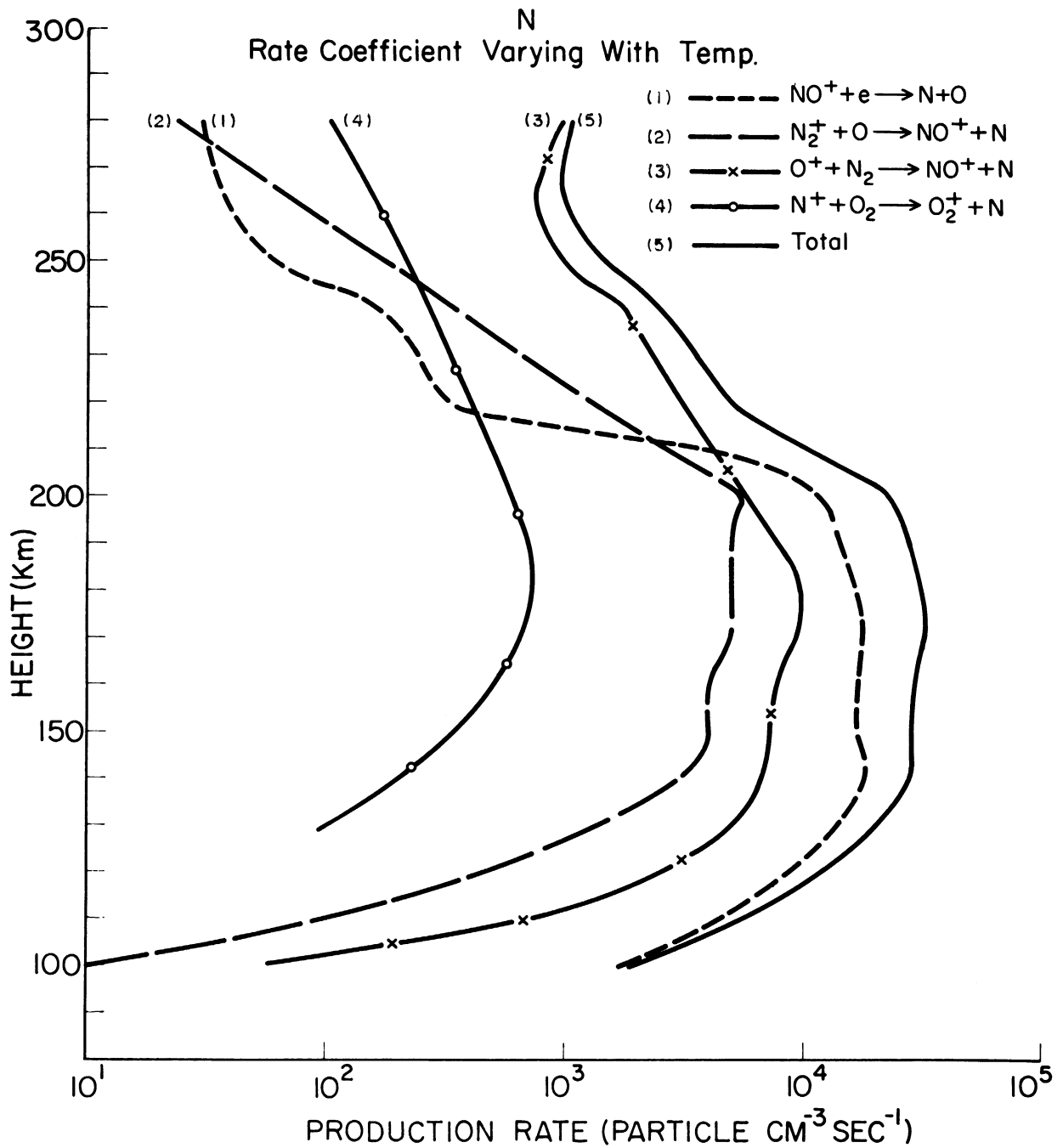


Fig. 5. Production rates of N-atoms by various reactions for rate coefficients varying with temperature.

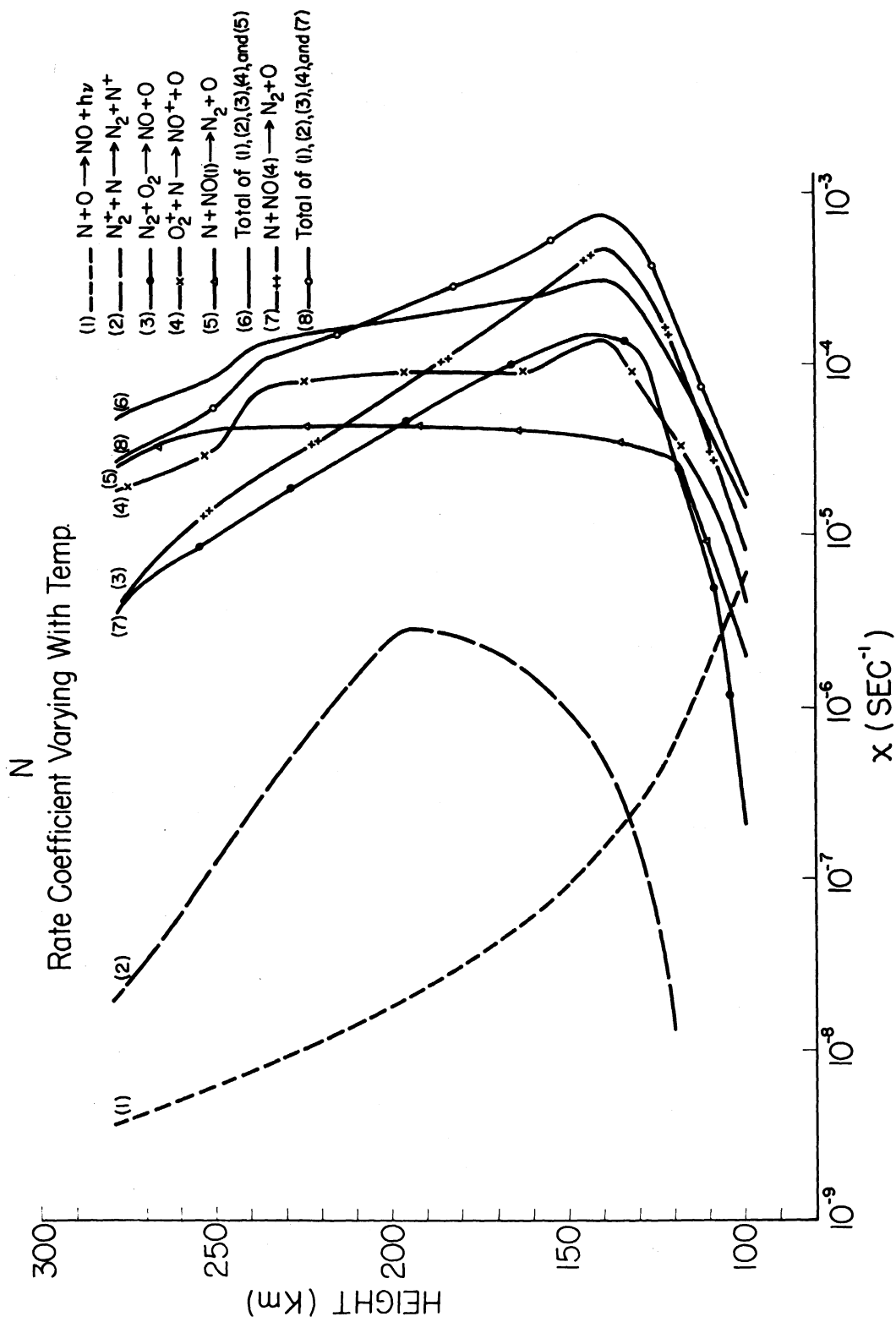


Fig. 6. Variation of  $x$  with altitude for two-body reactions having rate coefficients varying with temperature. Loss rate =  $x [N]$ . NO(1) and NO(4) represent NO density obtained from Curves (1) and (4) of Fig. 9, respectively.



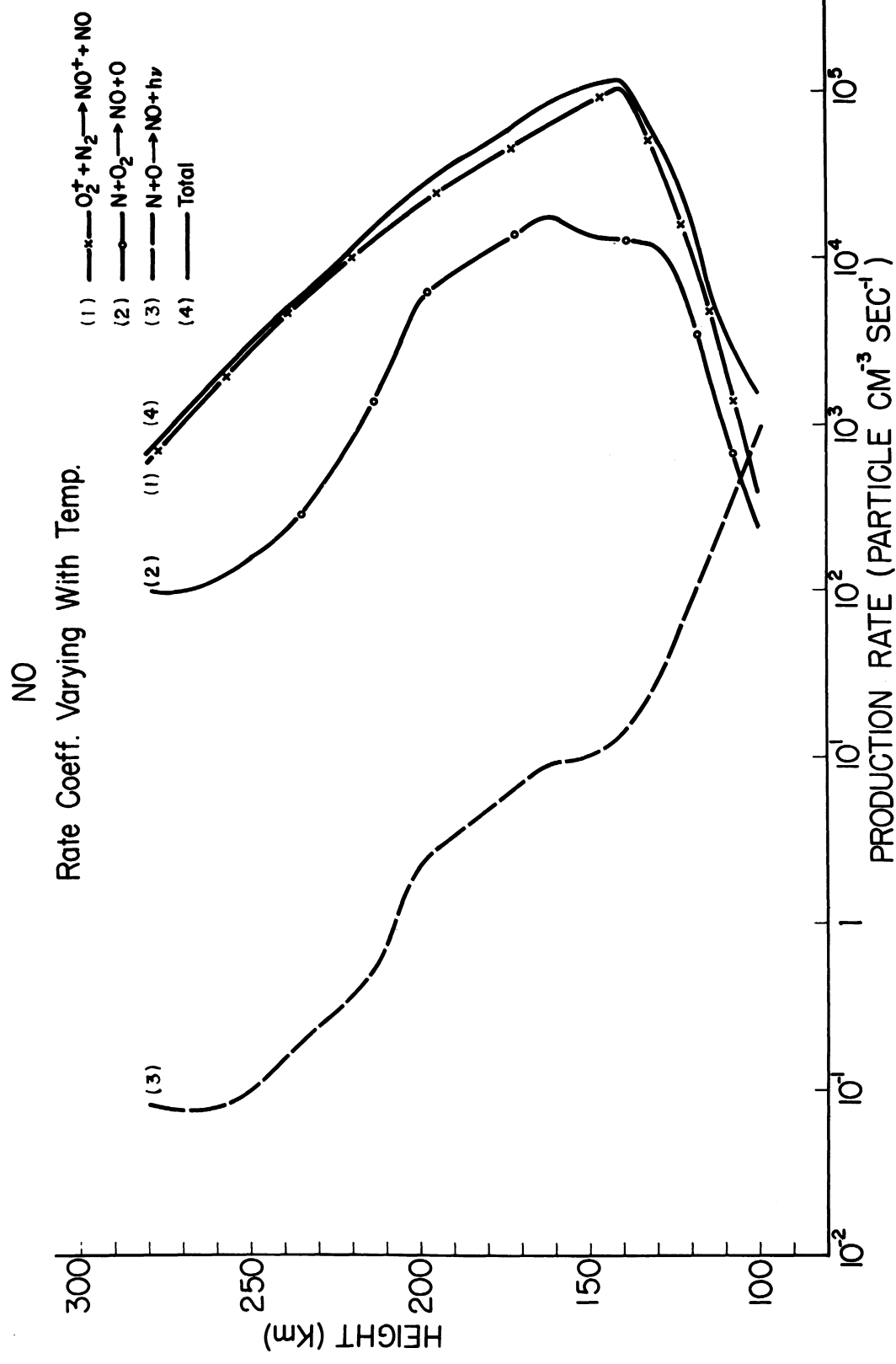


Fig. 7. Production rates of NO molecules by various reactions with rate coefficients varying with temperature.

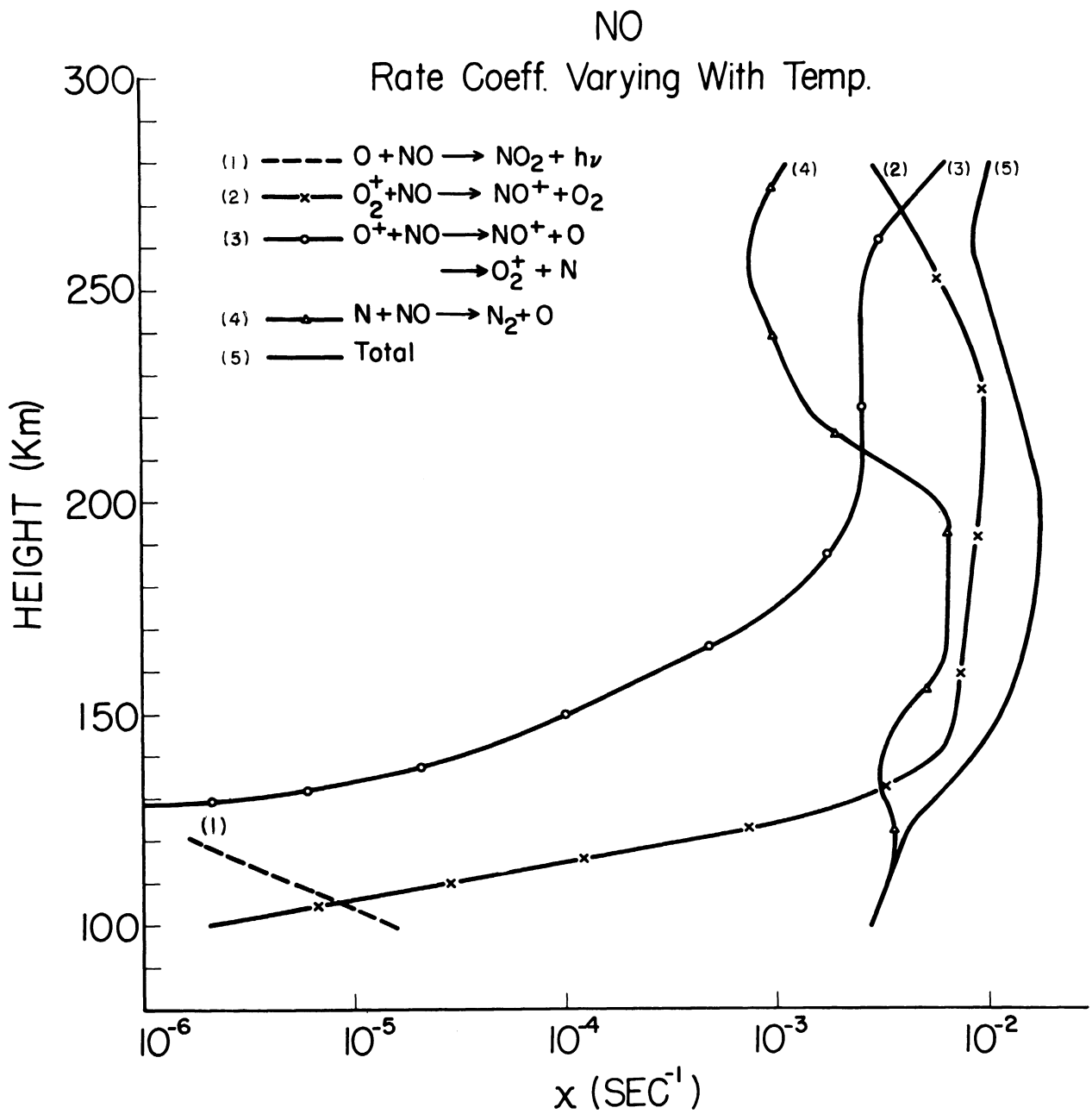


Fig. 8. Variation of  $x$  with altitude for various reactions having rate coefficients varying with temperature. To obtain loss rate of NO molecules, multiply  $x$  by  $[\text{NO}]$ .

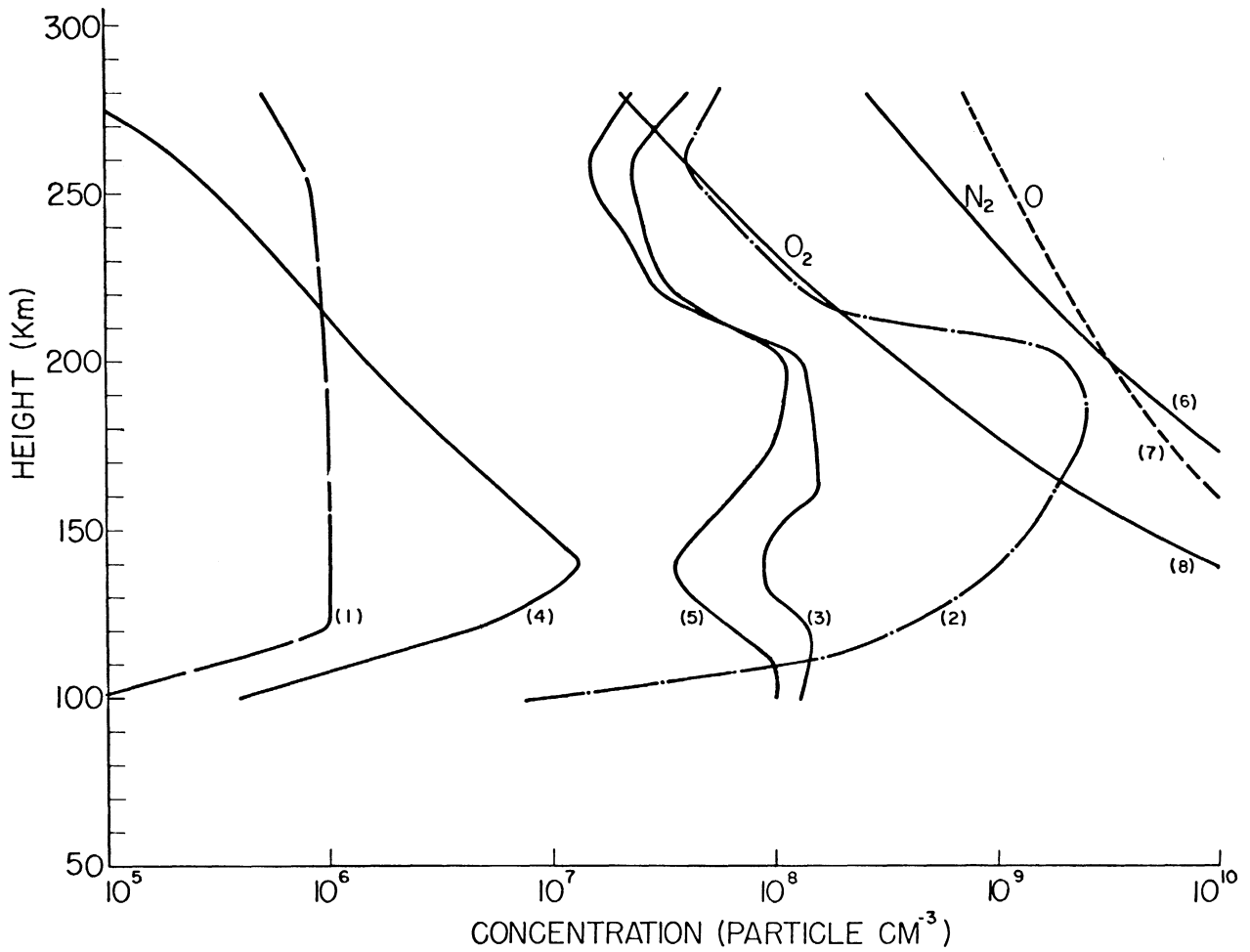


Fig. 9. Computed altitude distributions of N and NO. For comparison, the distributions of O, O<sub>2</sub> and N<sub>2</sub> obtained from CIRA 1965 are also shown. (1) Assumed NO distribution; (2) N distribution for (1) for constant rate coefficient; (3) N distribution for (1) for rate coefficient varying with temp.; (4) calculated NO distribution for (3) for rate coefficient varying with temp.; (5) N distribution calculated from (4); (6) N<sub>2</sub> distribution from CIRA 1965; (7) O distribution from CIRA 1965; (8) O<sub>2</sub> distribution from CIRA 1965.