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Les variations de la densité et du transport de chaleur par conduction dans l'atmosphère supérieure

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FOREWORD

"Aeronomic Chemical Reactions" is the text of a lecture I gave at the "Second International Symposium on the Physics and Medicine of the Atmosphere and Space" in San Antonia, Texas. This paper will be published in 1960 in a book entitled "Physics and Medicine of the Atmosphere and Space" Ed. Drs Otis O. Benson, Jr and Hubertus Strughold, John Wiley and Sons, New York.

AVANT-PROPOS

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VOORWOORD

"Aeronomic Chemical Reactions" is de tekst van een uiteenzetting welke ik gehouden heb op het "Second International Symposium on the Physics and Medicine of the Atmosphere and Space" te San Antonio, Texas, U.S.A. De tekst zal in 1960 verschijnen in een boek getiteld "Physics and Medicine of the Atmosphere and Space" Ed. Dr . Otis O. Benson, Jr and Dr Hubertus Strughold, John Wiley and Sons, New York.

VORWORT

"Aeronomic Chemical Reactions" ist der Text eines Exposé, das ich während des "Second International Symposium on the Physics and Medicine of the Atmosphere and Space" in San Antonio, Texas vorgestellt habe. Dieser Text wird in 1960 im dem Buch "Physics and Medicine of the Atmosphere and Space" Ed. Drs Otis O. Benson, Jr and Hubertus Strughold, John Wiley and Sons, New York, herausgegeben werden.

AERONOMIC CHEMICAL REACTIONS

by Marcel NICOLET

1. Introduction

The principal gases in the atmosphere, nitrogen and oxygen, are not transparent to radiation of short wave-lengths. Oxygen begins to dissociate at wave-lengths shorter than 2400 A, though the absorption of nitrogen is of great importance only at wave-lengths shorter than 750 A. To understand the photochemical and chemical equilibria it is necessary to know (a) what is the vertical distribution of gases; (b) their absorption coefficients for various wave-lengths; (c) the activation energies of various reactions; and (d) the number of solar photons available at different wave-lengths.

It has been shown by Chapman[1] that the dissociation of molecular oxygen has a very great importance and, therefore, that molecular oxygen must be transformed into atomic oxygen at great heights in the atmosphere. However, detailed investigation [2] shows that there are departures from photochemical and chemical equilibrium conditions and it is necessary to deal with transport phenomena in aeronomic problems.

2. Dissociation of Molecular Oxygen

2.1. The Theoretical Problem

In that the dissociation of molecular oxygen begins to appear, for increasing height levels, in the lower thermosphere one is no longer free to assume a constant molecular mass at these levels and, as a result, obtain a simple relation between the measured pressure and the temperature. In fact, vertical transport carries molecular oxygen upward while the atomic oxygen is carried downward since it tends to follow the hydrostatic distribution. Under these conditions, one dissociated O_2 molecule is replaced by another through the upward diffusion process while oxygen atoms are forced downward until they reach a region of sufficiently high pressure to cause them to recombine. Thus, it can no longer be assumed that the ratio $[n(O_2) + \frac{1}{2} n(O)] / n(N_2)$ remains constant through the whole thermosphere. It can only be applied below 100 km where the atomic oxygen concentration is less than the molecular oxygen concentration.

The dissociation of oxygen is obtained by photodissociation due to solar radiation[3] by the processes

$$O_2 + h\nu \quad (\lambda \leqslant 2424\ A) = 2O(^3P) \qquad (.1)$$

and

$$O_2 + h\nu \quad (\lambda \leqslant 1750\ A) = O(^3P) + O(^1D) \qquad (.2)$$

The absorption cross sections at the thresholds λ 2424 A and λ 1750A being of the order of 10^{-24} cm^2 and 10^{-19}cm^2, respectively, it is evident that the penetration of solar radiation for the two spectral regions will be very different.

The photolysis of ozone also produces oxygen atoms according to the process

$$O_3 + h\nu \rightarrow O_2 + O \qquad (.3)$$

There are two principal continua which lead to the dissociation of O_3. That of Chappuis, in the visible part of the spectrum from 4400 A to 7400 A, will first be considered. The more recent experimental data by Vigroux[4] show that variations of the absorption coefficient with the temperature are of the same order as the errors of photometric measurements. Therefore, the absorption coefficients measured at 291°K can be used for the computation of the rate of dissociation. The Hartley continuum in the ultraviolet also provides a very strong absorption which limits the penetration of solar radiation. This continuum is particularly important since it plays a role at wave-lengths shorter than 2400 A in the absorption by molecular oxygen. Due to the presence of O_3 molecules in the atmosphere, the rate of dissociation of O_2 is affected below 50 km.

The oxygen atoms produced by photochemical action (.1, .2 and .3) re-unite to form O_2 or unite with O_2 to form O_3. The formation of molecular oxygen can be the result of a three-body collision

$$O(^3P) + O(^3P) + M \rightarrow O_2 + M \qquad (.4)$$

where M signifies any third atmospheric molecule. The two-body collision

$$O(^3P) + O(^3P) \longrightarrow O_2 + h\nu , \qquad (.5)$$

in which the energy of association is involved in the emission, can be neglected for altitudes of less than 100 km.

In addition, a reaction between O_3 and O takes place according to the process

$$O + O_3 \longrightarrow O_2 + O_2 \qquad (.6)$$

which is a two-body collision reaction depending on the activation energy.

With processes (.1) to (.6) it is possible to write the equations governing the rates of change of the concentrations $n(O_2)$, $n(O)$ and $n(O_3)$. Let J_2 and J_3 denote the, respective, photodissociation rate coefficients of O_2 and O_3, k_1 and k_2 the, respective, recombination coefficients, and k_3 the coefficient of the reaction (.6) between O and O_3. The rates of change are, therefore, given by the following equations :

$$\frac{dn(O_2)}{dt} + n(O_2)J_2 + k_2n(M)n(O)n(O_2) = k_1n(M)n^2(O) + 2k_3n(O)n(O_3) + n(O_3)J_3 \qquad (.7)$$

$$\frac{dn(O)}{dt} + 2k_1n(M)n^2(O) + k_2n(M)n(O_2)n(O) + k_3n(O_3)n(O) = 2n(O_2)J_2 + n(O_3)J_3 \qquad (.8)$$

$$\frac{dn(O_3)}{dt} + n(O_3)J_3 + k_3n(O)n(O_3) = k_2n(M)n(O_2)n(O) \qquad (.9)$$

These three equations are not independent when the total number of oxygen atoms (free and attached) remains constant.

2.2. Photoequilibrium Conditions

A theoretical discussion may begin with consideration of the steady state. In this case[5]

$$n(O_3)/n(O) = k_2n(O_2)n(M)/\left[J_3 + k_3\, n(O)\right] \qquad (.10)$$

and

$$n^2(O) = n(O_2)J_2/k_1n(M) \left[1 + \frac{k_2k_3}{k_1J_3}\, n(O_2)\right] \qquad (.11)$$

When the second term in the bracket of the second member of (.11) is less than unity (just beneath and above the mesopause) the equation can be written

$$n^2(O) = n(O_2)J_2/k_1n(M) \qquad (.12)$$

i.e., the equilibrium of atomic oxygen with molecular oxygen is the primary factor in the photoequilibrium of ozone and oxygen. In addition, we may assume that, below 50 km, J_3 is larger than $k_3n(O)$ and (.10) can be also simplified. Therefore, in the stratosphere

$$n^2(O_3) = \frac{k_2}{k_3}\, n(M)n^2(O_2)\ \frac{J_2}{J_3} \qquad (.13)$$

corresponds to the photochemical equilibrium equation which has been used by several authors in studying the vertical distribution of ozone. In fact, this equation corresponds to aeronomic conditions where $k_1 n(M) n^2(O)$ is negligibly small and to an atomic oxygen concentration

$$n^2(O) = J_2 J_3 / n(M) k_2 k_3 \tag{.14}$$

(.13) and (.14) correspond to the conditions where $n(O_3) > n(O)$ and (.11) and (.12) to those in which $n(O) > n(O_3)$.

By use of the photochemical theory it is possible to explain a stratospheric peak in the vertical distribution of ozone. However, the actual behavior of stratospheric and tropospheric ozone is not explained since the observed geographical and seasonal trends in the amount of O_3 does not indicate a decrease from summer to winter and from equator to pole.

In view of the facts that, in the neighbourhood of the tropopause, the times involved are of the order of years (about 10 years between 15 and 20 km) and there is a great difference between tropospheric and stratospheric ozone amounts, it can be concluded that the time of ozone residence in the stratosphere is of the order of several years. In other words, the altitude of the ozone peak is not determined in the stratosphere by photochemical equilibrium conditions which are attained below 25 km after very long times but by the effect of mixing causing ozone molecules to follow the atmospheric distribution. It is clear that the time of residence in the stratosphere (just above the tropopause) must be very long, in general, for it must be of the order of the time of restoration of photoequilibrium conditions. Furthermore, since the conditions due to an overhead sun and the sun at the horizon lead to, respective, times of order of weeks and one year at 25km, it must be concluded that a meridional transport is possible before photochemical conditions are restored. It follows that a seasonal variation in ozone content is associated with a horizontal transport of ozone. Finally, it must be concluded that there is a mass exchange between the stratosphere and troposphere requiring a very long time (of the order of 10 years) and the discontinuities on the vertical distribution of ozone below the peak must deal with the stratospheric barrier.

2.3. The Peak of the Atomic Oxygen Concentration

The mesopause, being the level where a minimum of the temperature is reached, can be considered also as a border between two regions where the behavior of atomic oxygen is different. In the mesosphere atomic oxygen is subject to photochemical and chemical actions leading to different aeronomic conditions between day and night while its vertical distribution in the thermosphere depends on the downward transport[6] and its maximum concentration on the compensation between a production and recombination of the order of 4×10^{11} atoms $cm^{-2} sec^{-1}$. A concentration of the order of between 1×10^{12} and 2×10^{12} oxygen atoms in the neighborhood of 90-95 km will give a balance between dissociation and recombination, since at the production peak caused by photodissociation of molecular oxygen in the Schumann-Runge continuum the rate coefficient is about 1.5×10^{5} atoms $cm^{-3} sec^{-1}$. Furthermore, in photochemical equilibrium conditions, the concentration peak should be observed near 110-115 km and would correspond to a value of the order of 1.5×10^{12} atoms cm^{-3}. Such a concentration would correspond to about twice the nitrogen concentration, and, therefore, $n(O) = 1.5 \times 10^{12}$ should be considered as the maximum value which can be reached at 110-115 km.

It is clear that photo-equilibrium conditions lead to a modification of the ratio oxygen-nitrogen, which is kept constant in perfect mixing, namely (+)

$$\frac{n(O) + 2n(O_2)}{n(N_2)} = \frac{1}{2} \qquad (.15)$$

The condition of the constancy of the ratio oxygen-nitrogen has been applied to almost all atmospheric models. Such a hypothesis leads to a deficiency of atomic oxygen in the thermosphere when the observed concentration of molecular oxygen is taken into account in the computations.

(+) Exactly 0.5365. Such a hypothesis leads to a density $\rho = 1.3 n(N_2) m(N_2)$

However, such a restriction does not apply to aeronomic conditions for which transport is involved. First, the vertical distribution of atomic and molecular oxygen in the thermosphere above 100 km must correspond to a diffusion equilibrium. Second, the production of almost 10^{11} oxygen atoms per cm^2 sec above 100 km will modify the constancy of the ratio oxygen-nitrogen. Finally, the absolute values of the atomic oxygen concentration should be fixed by the secular equilibrium between the entire production of oxygen atoms and their recombination.

Considering that there is continuous transport and that

$$\int_z^{\infty} k_1 n(M)\ n^2(O)\ dz = \int_z^{\infty} n(O_2) J_2\ dz \qquad (.16)$$

it is possible to determine the normal conditions. If a mean value is adopted for n(O), we can write (.16) as

$$\overline{n^2(O)}\quad k_1 n(M) N = 2 \times 10^{11}\ cm^{-2} sec^{-1} \qquad (.17)$$

and $n(O) = 1.7 \times 10^{12}\ cm^{-3}$ between 90 and 100 km, i.e. at the production peak. Since such a concentration corresponds to the concentration peak in photochemical conditions we may adopt it as a conservative value. In Fig. 2 atomic oxygen concentrations representing photochemical equilibrium conditions between 85 km and 110 km are given. Concentrations obtained from (.17) which cannot be applied above the production peak show (see Fig. 2) that the maximum concentration of a layer, for which the thickness is of the order of the scale height, varies between $7 \times 10^{11} cm^{-3}$ at 85 km and $1.7 \times 10^{12}\ cm^{-3}$ at about 95km.

Comparing the possible concentrations of atomic oxygen between 100 km and 110 km, we see (Fig. 2) that two extreme values may be defined. The downward transport can lead to almost

$$n(O) = \frac{1}{10}\, n(N_2) \qquad (.18)$$

and the photo-equilibrium conditions to

$$n(O) = 2n\ (N_2); \qquad (.19)$$

i.e. an oxygen-nitrogen ratio greater than the constant mixing ratio (.15).

A constant mixing ratio would lead to a concentration peak just below 90 km (or 95 km) and essentially a vertical distribution above the peak almost following the atmospheric distribution. Such conditions would represent the extreme case dealing with a rapid downward transport due to mixing from 110 km to the mesopause.

Therefore, after considerimg extreme conditions, it appears that they are represented by a factor of 20 in atomic oxygen concentration at 110-115 km. In any event, the oxygen-nitrogen ratio cannot correspond to the mixing ratio in the transition region and, even more, cannot be kept as a constant; for there are temporal variations according to the rapidity of the downward flow of oxygen atoms compared with the time needed to reach photochemical conditions.

Since the peak of atomic oxygen is situated at such low heights and because its absolute concentration is subject to variations, the patchy and irregular nature of the airglow, and in particular, of the green line of OI, can now be understood as follows.

Firstly, confirmation of the Chapman theory attributing the emission of the green line to the threebody reaction

$$O + O + O \longrightarrow O_2 + O\,('S) \qquad (.20)$$

has been observed by rocket measurements (Berg, Koomen, Meredith, Scolnik[7]; Koomen, Scolnik, Tousey[8]; Heppner and Meredith[9]) between 85-90 km and 120 km.

However, in a quiescent atmosphere, it is not possible to determine how far fluctuations of the green line emission can be related to the variation of chemical and photochemical actions. Since the intensity fluctuations show that there is no fixed maximum in the daily variation, the most plausible inference to be drawn is that downward transport is responsible. Additional support is given to this idea by the variation of the intensity which can be more than 100 °/₀ of the mean intensity. Great significance must be attached to the transport of the patchiness of the green line, and it must be kept in mind that, in addition to the downward vertical transport of atomic oxygen, there is a latitudinal transport corresponding to a flow of atoms from the tropical regions to the dark polar regions and an opposite flow for molecular oxygen. This atomic or molecular flow is distributed by prevailing winds which, however, must lead to the transport of the patchiness of the emission. Nevertheless, the existence of the patchiness is associated with the downward vertical transport of oxygen atoms and the life time of characteristic features (maximum of intensity) is related to a deeper penetration than usual due to some atmospheric disturbance. Information regarding the latitudinal transport will be obtained by investigations along a meridian chain. First indications are given by the possibility of a very large variation of pressure at 100 km, namely between 1×10^{-4} mm Hg and 3×10^{-4}mm Hg.

3. Atomic Nitrogen and Nitric Oxide

3.1. Preliminary Considerations

The aeronomic problem of nitrogen, involving its dissociation, has been studied theoretically by Bates[10,11] in assuming a photochemical equilibrium and by Nicolet[12] by considering departures from equilibrium conditions. Nitric oxide was first considered as an effective constituent of the high atmosphere by Nicolet[13] when he discussed the possibility of its formation in order to explain the production of the ionospheric D layer by NO photoionisation. Various computations have been made on the nitrogen dissociation problem and several atmospheric models have been computed by using arbitrary figures for the dissociation of nitrogen (Rocket Panel[14]; Johnson[15] and Kallman, White and Newell[16]).

The aeronomic problem of nitrogen dissociation is very difficult since it depends on several processes for which the rate coefficients are not well known. Since Nicolet's analysis[13], several new experimental determinations have been made which are of importance for the analysis of the processes affecting the equilibrium between atomic nitrogen and nitrogen oxides. In fact, the behavior of nitrogen oxides depends on the dissociation of molecular nitrogen and it is necessary to determine the conditions in the mesosphere and the thermosphere by delineating the equilibrium conditions and departure from equilibrium which can exist.

3.2. Dissociation of Nitrogen

The dissociation of nitrogen molecules (Bates [11]) is due to the predissociation mechanism to which attention was drawn by Herzberg and Herzberg [17];

$N_2(X^1\Sigma_g^+)$ + $h\nu$ $(\lambda\lambda \sim 1200 - 1250A)^{(+)} \longrightarrow N_2(a'\pi_g)$ (.21)

$N_2(a'\pi_g) \longrightarrow 2N$

This process [11] should have a rate coefficient J_{N_2} at zero optical depth (altitude $\gg$ 90 km) of the order

$$J_{N_2} \leqslant 10^{-12} \text{ sec}^{-1} \qquad (.22)$$

This rate coefficient must decrease very rapidly with decreasing height due to the absorption of molecular oxygen which has a very complicated structure in this spectral range.

If dissociative recombination is effective, i.e.

$$N_2^+ + e \longrightarrow N + N \qquad (.23)$$

for which the recombination coefficient, α_{N_2}, may be between [18]

$$\alpha_{N_2} = 10^{-7} \text{ to } 10^{-6} \text{ cm}^3\text{sec}^{-1} \qquad (.24)$$

the photoionization processes by ultraviolet radiation and X-rays

$$N_2 + h\nu \longrightarrow N_2^+ + e$$

must be considered as leading to dissociation of nitrogen in the various ionospheric layers.

Since molecular nitrogen is ionized by ultraviolet radiation of λ <796 A and by shorter wavelengths λ <661 A, for which the absorption coefficient is between 1 and 2 x 10^{-17} cm^2 (Waifan, Walker and Weissler[19] ; Curtiss [20]; Astoin and Granier[21]), only 5 x 10^8 photons cm^{-2} sec $^{-1}$ are needed in order to obtain an ionization-rate coefficient of 10^{-8}sec^{-1} at zero optical depth.

(+) In fact, there are three Lyman-Birge-Hopfield bands which are involved in this absorption process; namely (7-0) at 1250 A (8-0) at 1226 A and (9-0) at 1205 A. The, respective, absorption coefficients (in molecular oxygen) are about 1.5x10^{-18}cm^2, 4x10^{-19} cm^2 and 1.5x10^{-17}cm^2. Therefore, the penetrating radiation corresponds to 1226 A, for which the unit optical depth is reached near 90 km.

The unit optical depth for such ultraviolet radiation occurs at 160-170 km (F layer peak) for an overhead sun, and it should be at about 300 km at sunset.

Furthermore, X-ray action is another mechanism which can occur in the D and E layers. According to Byram, Chubb and Friedman[22] the number of X-ray photons available for the ionization of the E layer is of the order of 5×10^8 cm^{-2}sec^{-1}. Below 100 km the X-ray ionization is associated with solar disturbances [23] and can lead to low activities from 10^3 to 10^6 photons cm^{-2}sec^{-1} at $\lambda \leqslant 8$A. Therefore, a comparatively large N_2^+ concentration could occasionally be established near the mesopause level.

3.3. Primary Formation of Nitrogen Oxide

Since there is a nitrogen dissociation process in the lower thermosphere, we must consider the following three-body collision process

$$N + O + M \rightarrow NO + M \qquad (.25)$$

for which the rate coefficient

$$b_1 = 5 \times 10^{-34}\ T^{1/2}\ \text{cm}^6\text{sec}^{-1} \qquad (.26)$$

is assumed. At 400°K, $b_1 = 10^{-32}$ cm^{6}sec^{-1}, but this is only an order of magnitude. The variation with temperature, assumed to be proportional to $T^{1/2}$, corresponds to the kinetic velocity.

3.4. Formation of Nitrogen Dioxide

Reaction (.21) leading to NO formation and reactions involving nitric oxide and atomic oxygen must also be considered. First, the formation of the product NO_2 according to the process

$$NO + O \rightarrow NO_2 + h\nu \qquad (.27)$$

of which the rate-coefficient b_2 depends on the emission probability of the radiative process, should be noted. The kinetic energy must be transformed into potential energy and this change must take place during the collision time. The rate coefficient b_2 may be written as follows

$$b_2 = \sigma^3 \quad GA_{ji} \quad cm^3 sec^{-1} \qquad (.28)$$

in which σ is the effective collision diameter, G the statistical weight factor or the ratio of the electronic level considered for recombination with those of all the possible electronic levels, and A_{ji} the spontaneous probability of emission of the electronic transition corresponding to recombination.

The formula (.28) was written in considering, as a rough approximation, that the time of collision depends only on the collision diameter and on the relative mean velocity. An effective collision diameter of 1.5 A will give $b_2 = 10^{-23} GA_{ji}$ $cm^3 sec^{-1}$ and one of 3.2 A will give $b_2 = 10^{-22}$ GA_{ji}.

As far as the factor GA_{ji} is concerned no precise value can be obtained, for the states of nitrogen dioxide are not known for the computation of the statistical weight factor G. However, Neuberger and Duncan[24] determined a mean life time of the order of 2.6×10^{-7} sec for a transition corresponding to the inverse process of absorption as measured by Hall and Blacet[25]. Since this life time corresponds to the minimum value of the oscillator strength, and as the value of the effective collision diameter can be fixed arbitrarily, we can write

$$b_2 = 10^{-16} \ cm^3 sec^{-1} \qquad (.28a)$$

noting that this tentative estimate is very crude and the possible error may be of an order of magnitude. Values of $10^{-17} cm^3 sec^{-1}$ or 10^{-15} cm^3 sec^{-1} cannot be rejected a priori, but it seems that b_2 as given by (.28a) is, at the present time, the best value available for use as a working value for the chemosphere. In fact, recent measurements made by Kaufman[26] lead to possible values between $5 \times 10^{-18} cm^3 sec^{-1}$ and $1.2 \times 10^{-16} cm^3 sec^{-1}$.

A three-body collision

$$NO + O + M \rightarrow NO_2 + M \qquad (.29)$$

should also be considered since it represents the limiting process of formation of nitrogen dioxide at relatively high pressures. Kaufman, Gerri and Bowman [27] gave a value of about $2 \times 10^{-32} \mathrm{cm}^6 \mathrm{sec}^{-1}$ in their study of the role of nitric oxide in the thermal decomposition of nitrous oxide, and Ford and Endow [28] found, for nitrogen as a third body, a value of 5×10^{-32} $\mathrm{cm}^6 \mathrm{sec}^{-1}$ at 300°K assuming an $O + O_2$ reaction. Recent data [26] lead to 5.5×10^{-32} $\mathrm{cm}^6 \mathrm{sec}^{-1}$ when the third body is molecular nitrogen. Therefore, reaction(.29) would require 4×10^{15} nitrogen molecules before it could successfully compete with (.27).

The rapid reactions

$$NO + O \longrightarrow NO_2^* \qquad (.30)$$

and

$$NO_2^* \longrightarrow NO + O \qquad (.31)$$

competing with

$$NO_2^* \longrightarrow NO_2 + h\nu \qquad (.32)$$

introduced by Kistiakowsky and Volpi [29] in their analysis of the reactions of nitrogen atoms correspond, respectively, to a reaction with almost a normal coefficient rate of the order of $10^{-10} \mathrm{cm}^3 \mathrm{sec}^{-1}$ and a probability of the order of 5×10^8 to 5×10^9 sec^{-1}. With such values and also with data from Kaufman, Gerri and Bowman[27] one can expect a strong tendency towards the greatest possible value for the rate coefficient (.28), namely 10^{-15} $\mathrm{cm}^3 \mathrm{sec}^{-1}$, when about $10^{-2} n(NO_2)$ or $10^{-3} n(NO_2)$ emit fluorescence.

3.5. Dissociation of Nitrogen Dioxide

In any case, if there is formation of NO_2, it is important for aeronomic purposes to determine the principal processes of dissociation of nitrogen dioxide. Firstly, the photodissociation process

$$NO_2 + h\nu \longrightarrow NO + O \qquad (.33)$$

has a high rate coefficient, J_{NO_2}, which was estimated by Bates[11] to be

$$J_{NO_2} = 5 \times 10^{-3} \mathrm{sec}^{-1} \qquad (.34)$$

The reaction

$$O + NO_2 \longrightarrow NO + O_2 \qquad (.35)$$

has a rate coefficient b_3 which has been determined recently from laboratory measurements by Kistiakowsky and Volpi [29] and Ford and Endow [28]. The lower limit at 300° K is $2 \times 10^{-12} cm^3 sec^{-1}$ and may be about $4 \times 10^{-12} cm^3 sec^{-1}$.

Adopting a general formula for two-body reactions as follows

$$b = f \times 1.5 \times 10^{-11} T^{1/2} e^{-E/RT} \qquad (.36)$$

in which f is an equivalent steric factor and E the activation energy, (.35) can be interpreted with $f = 0.3$ and $E = 2.0$ kcal. An equivalent steric factor in the range $f = 0.1$ to 1 will lead to activation energies of about 1.2 to 2.5 kcal/mole. Therefore, we can adopt here the tentative estimate

$$b_3 = 5 \times 10^{-12} T^{1/2} e^{-2000/RT} \qquad (.37)$$

It must be pointed out that the probability of reaction (.35) was taken as 10^{-5} per collision at a temperature of 300° K (Spealman and Rodebush [30]) and with a steric factor of 0.01 leads to an activation energy not less than 4 kcal/mole. Nicolet [12] considering lower activation energies, i.e. 3 kcal for such reactions was led to adopt very low steric hindrance in order to follow experimental data. In fact, theoretical difficulties which were involved in the aeronomic problem of nitrogen oxides are being removed by using low activation energies.

3.6. Nitric Oxide and Ozone

If nitric oxide is present in sufficient concentration in the mesosphere, the following reaction with ozone takes place

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad (.38)$$

for which the correct order of magnitude of the rate coefficient b_4 can be given [31] as

$$b_4 = 7.5 \times 10^{-14} T^{1/2} e^{-2400/RT} \qquad (.39)$$

This gives a steric factor $f = 0.05$ in formula (.36).

3.7. Nitrogen Dioxide and Atomic Nitrogen

In addition, atomic nitrogen can react with nitrogen dioxide as follows

$$N + NO_2 \rightarrow NO + NO \quad (.40a)$$
$$\rightarrow N_2O + O \quad (.40b)$$
$$\rightarrow N_2 + 2O \quad (.40c)$$

According to Spealman and Rodebush[30] the rate coefficient b_5 of (.40a) is of the same order of rapidity at 40°C as that of (.35) between nitrogen peroxide and oxygen atoms. However, recent experimental evidence shows that several orders of magnitude may be involved and it is difficult to make precise application in aeronomic problems.

Harteck [32] considered reactions (.40b) and (.40c). He adopted an activation energy for (.40a, b, c) of the order of 4 kcal and the following values for b_5 at 300°K:

$$b_{5a} = 5 \times 10^{-15} cm^3 sec^{-1}; \; b_{5b} = 3 \times 10^{-15} cm^3 sec^{-1};$$
$$b_{5c} = 2 \times 10^{-15} cm^3 sec^{-1} \quad (.41)$$

According to recent results of Kistiakowsky and Volpi[29] b_{5b} at room temperature, which should be

$$6 \times 10^{-15} < b_{5b} < 6 \times 10^{-12} cm^3 sec^{-1} \quad (.42)$$

may correspond to the values adopted by Harteck. Therefore, it is certain that (.40) is less important than (.35); particularly at the mesopause level.

3.8. Nitric Oxide and Atomic Nitrogen

The most important process is the reaction between atomic nitrogen and nitric oxide since it must be the principal process leading to nitrogen recombination

$$N + NO \longrightarrow N_2 + O \qquad (.43)$$

A relatively precise value for the rate coefficient, b_6 of this process has been dertermined very recently. In a general study of the kinetics of formation of nitric oxide in the temperature range from 2000°K to 3000°K Glick, Klein and Squire[33] found that

$$O + N_2 \rightleftharpoons NO + N \qquad (.44)$$

lead to an activation energy of 74 ± 5 kcal for the step $O + N_2 \rightarrow NO + N$ for which the heat of reaction is 75.8 kcal and, therefore, that the activation energy for the reverse step (.43) is approximately zero. Furthermore, Kistiakowsky and Volpi[29], in a first study of reactions of nitrogen atoms with oxygen and nitrogen oxides, have shown that reaction (.43) is very fast and that its lower limit is $b_6 \geqslant 6.6 \times 10^{-13} cm^3 sec^{-1}$. In that case the activation energy of (.43) should be less than 3.5 kcal. In order to utilize a rate coefficient consistent with the general formula (.36) used in the present investigation we should adopt

$$b_6 = 1.5 \times 10^{-12} T^{1/2} e^{-2000/RT} cm^3 sec^{-1} \qquad (.45)$$

However, in a recent paper, Kistiakowsky and Volpi[34] consider that b_6 should be greater than $8 \times 10^{-11} cm^3 sec^{-1}$. Such a high rate leads to a very low value of the activation energy (maximum 0.5 kcal). Therefore, we use the following formula

$$b_6 = 1.5 \times 10^{-11} T^{1/2} \qquad (.45a)$$

It may be pointed out that the activation energy for the above is less than 0.5 kcal and the possible variation would lead to an underdetermination of the rate coefficient by an order of magnitude at the mesopause level. Nevertheless, any error in the numerical value of (.45a) would not appear to change the general picture but will simply modify the absolute values of nitric oxide concentration in the atmospheric region where the temperature is very low. In other words, any value given for n(NO) is approximate to an order of magnitude.

3.9. Atomic Nitrogen and Molecular Oxygen

Another reaction which has not been considered before is

$$N + O_2 \longrightarrow NO + O \qquad (.46)$$

since its rate coefficient, b_7, requires an excessively high activation energy at the mesopause level. However, in the thermosphere, it is necessary to consider all reactions involving nitrogen atoms which lead to the formation of nitric oxide. In fact, Harteck[32] has drawn attention to this reaction for chemospheric processes and has adopted a rate coefficient of the order of 10^{-16} with an activation energy equal to 6 kcal.

Since the analysis of Vetter [35] and Wise and Trech [36] of reaction (.46) and its reverse, for which the energy of dissociation used was 170 kcal instead of 225 kcal, Haufman and Kelso[37] have recently interpreted data on the thermal decomposition of nitric oxide within one consistent mechanism. Considering again the reaction

$$O + NO \rightleftarrows N + O_2, \qquad (.47)$$

which is endothermic by 32 kcal when nitrogen atoms are formed and should have an activation energy of 40 kcal or more, the reverse reaction (.46) would, therefore, have an activation energy not less than 8 kcal. Such a value shows that (.43) is about 100 times faster at 1500°K than (.47). However, the rate coefficient b_7 as determined between 400° K and 500° K by Kistiakowsky and Volpi[29] gives 6.2 kcal for the activation energy. A comparison between these two experimental results shows that there is a small difference near 400° K but a factor of ten at 1500° K. Since Kistiakowsky and Volpi's data have been determined for the lowest temperature we represent b_7 by

$$b_7 = 1.5 \times 10^{-13} T^{1/2} e^{-6200/RT} \qquad (.48)$$

Comparing the rate coefficients of (.47) and (.48) we obtain the ratio

$$\frac{b_7}{b_6} = 10^{-2} \times e^{-6200/RT} \qquad (.49)$$

which will lead to the determination of the nitric oxide concentration in the thermosphere. It can be seen that the exponential factor must be known accurately in order to obtain an exact value even if there is a systematic error in the pre-exponential factor. Therefore, no reliance can be placed on detailed numerical results, for only order-of-magnitude calculations can be obtained from experimental results for aeronomic problems.

3.10. Nitrogen Dioxide Equilibrium Conditions

Considering all chemical processes in which nitrogen dioxide is involved, the differential equation for NO_2 may be written as follows :

$$\frac{dn(NO_2)}{dt} = -n(NO_2)\left[b_3 n(O) + b_{5a,b,c} n(N) + J_{NO_2} \right] + n(NO)\left[b_2 n(O) + b_4\, n(O_3) \right] \qquad (.50)$$

During the day, a photo-equilibrium must exist and, therefore, the equation (.50) becomes, with

$$\frac{dn(NO_2\ )}{dt} = 0,$$

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2 n(O) + b_4 n(O_3)}{J_{NO_2} + b_3 n(O) + b_{5a,b,c,} n(N)} \qquad (.51)$$

Inserting numerical values in (.51), we see that $n(NO_2)$ is only a fraction of $n(NO)$ for

$$\frac{n(NO_2)}{n(NO)} = \frac{10^{-16}\ n(O) + (1.3 \pm 1.0) \times 10^{-12}\ n(O_3)}{5 \times 10^{-3} + (9 \pm 7) \times 10^{-14}\ n(O)} \qquad (.52)$$

cannot be greater than unity in the mesosphere and the thermosphere (see Fig. 3).

The photodissociation of NO_2 plays a role below 40 km in the stratosphere and, therefore, the practical ratio is given by

$$\frac{n(NO_2)}{n(NO)} = \frac{b_4 n(O_3)}{J_{NO_2}} \simeq 2 \times 10^{-12} \quad n(O_3) \qquad (.52a)$$

which is greater than unity where $n(O_3) > 5 \times 10^{11} \text{cm}^{-3}$.

In the upper stratosphere (> 40 km) and in the mesosphere, the day nitrogen dioxide-nitric oxide ratio is given by

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2}{b_3} + \frac{b_4 n(O_3)}{b_3\, n(O)} \qquad (.52b)$$

This shows (see Fig. 4) that nitric oxide cannot be transformed into nitrogen dioxide in the mesosphere for $n(NO_2)/n(NO)$ varied from 10^{-2} to 10^{-4}

In the thermosphere, there is no practical difference, due to nitrogen dioxide formation, between day and night concentration, for

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2}{b_3} \qquad (.52c)$$

After twilight, the nitrogen dioxide-nitric oxide ratio must increase in the mesosphere since ozone acts efficiently in the formation of nitrogen dioxide during dark hours. The night equilibrium conditions are given by

$$\frac{n(NO_2)}{n(NO)} = \frac{b_4 n(O_3)}{b_3 n(O)} > 1 \qquad (.52d)$$

when concentration of atomic oxygen is sufficiently small, namely $n(O)/n(O_3) < (b_4/b_2) \simeq 10^{-4}$.

3.11. Nitric Oxide Equilibrium Conditions

Since there is a day equilibrium between nitric oxide and nitrogen dioxide, the equation governing the rate of change of the concentration of n(NO) is

$$\frac{dn(NO)}{dt} = -n(NO)\left[I_{NO} + J_{NO} + b_6 n(N)\right] + \left[b_1 n(M) \; n(O) + b_7 n(O_2)\right] n(N) \qquad (.53)$$

The conditions for the day equilibrium can be conveniently written as

$$\frac{n(NO)}{n(N)} = \frac{b_1 n(M) n(O) + b_7 \, n(O_2)}{J_{NO} + b_6 \, n(N) + I_{NO}} \qquad (.54)^{(+)}$$

In (.53) and (.54) we have added the loss process of nitric oxide which has not been considered above; namely

$$NO + h\nu \;\; (\lambda \sim 1900 \text{ A}) \longrightarrow N + O \qquad (.55)$$

for which Bates [11] has adopted a rate coefficient, J_{NO}, of

$$J_{NO} = 10^{-7} \;\; \sec^{-1} \qquad (.56)$$

As Bates has pointed out, this value results from crude estimates and must be considered very approximate.

Furthermore, the photoionization

$$NO + h\nu \;\; (\lambda = 1216 \text{ A}) \longrightarrow NO^{+} + e \qquad (.57)$$

is also a loss process of neutral nitric oxide and is introduced in (.53). The ionization coefficient rate I_{NO} depends on the number of solar photons available in Lyman-alpha. According to values given by Friedman[38], I_{NO} can attain values greater than J_{NO}. Six ergs cm^{-2} sec^{-1} would give

$$I_{NO} = 7.6 \times 10^{-7} \;\; \sec^{-1} \qquad (.58)$$

(+) $b_1 n(M) n(O)$ will be neglected in the following paragraphs since it is generally negligible compared with $b_7 n(O_2)$.

If low values of less than one erg $cm^{-2}sec^{-1}$ observed at the minimum of solar activity are not correct, (.58) may be adopted as a normal value.

If numerical values of the various parameters involved in (.54) are as assumed, it can be shown that the term $b_7 n(O_2)$ in the numerator of (.54) is generally more important than $b_1 n(M) n(O)$. However, in the low temperature region centered on 85 km, the three-body association(+) would be a mechanism of nitric formation if $T \leqslant 150° K$.

A knowledge of n(NO) cannot be obtained from (.54) without discussing the formation of atomic nitrogen. However, in photochemical equilibrium conditions, it is possible to write (.54) as follows

$$\frac{n(NO)}{n(N)} \leqslant \frac{b_7\ n(O_2)}{J_{NO} + I_{NO}} \qquad (.59)$$

which shows the limiting ratio of nitric oxide and atomic nitrogen concentrations in a sunlit atmosphere. During the night, (.54) becomes

$$n(NO) = \frac{b_7}{b_6}\ n(O_2) \qquad (.60)$$

which can be applied to day conditions where $J_{NO} + I_{NO} < b_6 n(N)$.

As need scarely be emphasised, nitric oxide can only be obtained if atomic nitrogen existed. Nevertheless, attention must be drawn to the downward vertical transport of nitric oxide at the mesopause level.

3.12. Life Time of Nitric Oxide

In the mesosphere, there is practically no generation of atomic nitrogen and the loss process of nitric oxide is the reaction with atomic nitrogen. Equation (.54) becomes

$$\frac{n(NO)}{n(N)} = \frac{b_7 n(O_2)}{I_{NO}+J_{NO}} \qquad (.61)$$

and the final loss process for nitric oxides is

$$-\frac{dn(NO)}{dt} = b_6 n(N) n(NO) = n(N_2) J_{N_2} \qquad (.62)$$

which can be written, using (.61),

$$-\frac{dn(NO)}{dt} = -\frac{b_6 (J_{NO} + I_{NO})}{b_7 n(O_2) + b_1 n(M) n(O)} \, n^2(NO) \qquad (.63)$$

If $n_o(NO)$ is the concentration of nitric oxide at time $t = 0$, the solution of (.63) is

$$\frac{n(NO)}{n_o(NO)} = \frac{1}{1 + \frac{b_6 \, (J_{NO} + I_{NO})}{b_7 n(O_2) + b_1 n(M) n(O)} \, t} \qquad (.64)$$

and the time, τ_{NO}, to reduce the initial concentration of nitric oxide to 50 °/₀, i.e. the life time of NO, is

$$\tau_{NO} = \frac{b_7 \, n(O_2)}{b_6 (J_{NO} + I_{NO})} \quad \frac{1}{n_o(NO)} \qquad (.65)$$

Considering, first, the stratopause where $J_{NO} = 10^{-7}$ sec^{-1} and $I_{NO} = 0$, it can be seen that the life time of nitric oxide, τ_{NO}, is

$$\tau_{NO} = 7.6 \times 10^{15} / \, n_o \, (NO) \qquad (.66)$$

i.e. a very long time since the concentration of n_o (NO) should be very small.

Near the mesopause, where $J_{NO} + I_{NO} = 8.6 \times 10^{-7}$ sec^{-1}, the life time of nitric oxide becomes

$$\tau_{NO} = 1.4 \times 10^{11} / n_o(NO), \qquad (.67)$$

and it can be concluded that even a small concentration such as $n_o(NO) = 5 \times 10^4$ cm^{-3} cannot be maintained more than one month. In other words, if there is a vertical transport of nitric oxide, the limiting value at 80 km $n(NO) \simeq 10^5$ cm^{-3} is reduced to 50 °/₀ in not more than 15 days. Thus, a concentration of nitric oxide of the order of 10^{-10} of the total concentration can be maintained during one month at 80 km.

Consequently, the production of nitrogen atoms must be studied at and above the mesosphere before deducing the behavior of nitric oxide in the mesosphere.

3.13. Atomic Nitrogen near the Mesopause.

Using the set of reactions written above, the equation governing the rate of change of atomic nitrogen is

$$\frac{dn(N)}{dt} = 2n(N_2)J_{N_2} + n(NO)\,(J_{NO} + I_{NO}) - n(N)\left[b_6 n(NO) + b_7 n(O_2)\right] \qquad (.68)$$

Assuming a photoequilibrium (.68) becomes

$$n(N) = \frac{n(N_2)\,J_{N_2} + n(NO)\left[J_{NO} + I_{NO}\right]}{b_7 n(O_2)} \qquad (.69)$$

Adopting $J_{N_2} = 10^{-12}\,\text{sec}^{-1}$ at zero optical depth (.22), the concentrations of atomic nitrogen and nitric oxide can be deduced after using the concentrations of nitrogen and oxygen molecules of preceding chapters. The results are given in Table I.

Table I. Atomic Nitrogen and Nitric Oxide concentrations in Equilibrium Conditions. Predissociation of Nitrogen.

Altitude (km)	$n(N)$ (cm^{-3})	$n(NO)$ (cm^{-3})	$n(N_2)$ (cm^{-3})
80	5.5	3.9×10^{3}	3.3×10^{14}
82.5	4.7×10^{3}	1.0×10^{4}	2.2×10^{14}
85	8.6×10^{5}	2.9×10^{4}	1.5×10^{14}
87.5	2.2×10^{6}	2.4×10^{4}	9.3×10^{13}

Table I. (Contd.)

Altitude (km)	$n(N)$ (cm^{-3})	$n(NO)$ (cm^{-3})	$n(N_2)$ (cm^{-3})
90	3.3×10^{6}	2.1×10^{4}	5.9×10^{13}
92.5	4.2×10^{6}	1.7×10^{4}	3.8×10^{13}
95	4.4×10^{6}	1.4×10^{4}	2.5×10^{13}
97.5	4.0×10^{6}	1.3×10^{4}	1.6×10^{13}
100	3.7×10^{6}	1.0×10^{4}	1.1×10^{13}

From the numerical results shown in Table I, corresponding to the minimum possibilities for nitrogen dissociation, several conclusions can be reached. First, between 85 and 100 km, the limiting value of the nitric oxide concentration is reached and corresponds to equation (.60).

Any increase in the atomic nitrogen concentration will maintain this value and any increase below 85 km should lead to an increasing concentration of NO. Furthermore, the times for nitric oxide to reach the equilibrium conditions are less than one hour, if atomic nitrogen keeps its photo-chemical equilibrium value. Since it is certain that between one and two nights are required to reduce to 50 °/o the equilibrium value of atomic nitrogen concentration, equilibrium conditions can be considered as normal conditions.

Below the mesopause, for example at 82.5 km, the life time of nitric oxide increases while that of atomic nitrogen decreases. This is due to the fact that the life time of atomic nitrogen depends on the concentration of molecular oxygen and that of nitric oxide is subject to the variation of the concentration of atomic nitrogen. Therefore, there is practically an equilibrium for atomic nitrogen. No vertical transport should be considered for this atom and mixing cannot increase the atomic nitrogen concentration below the mesopause except during extremely short periods.

However, the conditions for the vertical distribution of nitric oxide are completely different. There may be a downward transport since the life time is related to the initial concentration according to equation (.67). Consequently, since the life time increases downwards, below 80 km nitric oxide should be distributed according to the atmospheric distribution.

4. Ionospheric Effects on Chemospheric Processes

4.1. Effects of Dissociative Recombination

The effect of dissociative recombination would be easy to determine if charge transfer were not operative for molecular nitrogen ions. Unfortunately, it is impossible to obtain even an approximate value of the cross sections at the low energies existing in the ionosphere.

Bates[39] has shown that N_2^+ ions have a short life time in the ionosphere, for spectral observations of the twilight airglow spectrum requires a rapid loss of these ions. An absence of ionising radiation cannot be accepted since X-rays ionize both nitrogen and oxygen. Therefore, it seems reasonable to consider that dissociative recombination is a process which may be rapid, i.e.

$$N_2^+ + e \longrightarrow N + N \qquad (.70)$$

with a recombination coefficient

$$\alpha = 10^{-7} \text{ to } 10^{-6} \text{ cm}^3 \text{ sec}^{-1} \qquad (.24)$$

Since the electronic concentration in the E and F layers is between 10^5 and 10^6 cm^3, the life time, $\tau_{N_2^+}$, of molecular nitrogen ions (to reduce the molecular ion concentration to 50 °/₀ of the initial value) should be

$$\tau_{N_2^+} \leqslant 1 \text{ minute} \qquad (.71)$$

If dissociative recombination can be applied in the low thermosphere, the ionization by X-rays in the spectral range 35-60A is available for the production of nitrogen atoms. Using data of Byram, Chubb and Friedman[22] for photoionization followed by dissociative recombination it can be expected that the number of nitrogen atoms liberated would not be less than $10^2 cm^3 sec^{-1}$. Comparing with the Herzberg-Herzberg mechanism giving about 10 atoms cm^3 sec^{-1} at 100 km, the degree of dissociation by photoionization of N_2, followed directly by dissociative recombination, should definitely be a powerful source of production of nitrogen atoms. Furthermore, Chubb, Friedman, Kreplin, and Kupperian[23] observed 4×10^5 photons $cm^{-2}sec^{-1}$ in the spectral range 8 A to 20 A for a quiet sun, which indicates that few nitrogen atoms can be liberated during normal solar conditions below 100 km. On the other hand as long as the sun is quiet, X-rays cannot lead to a large production of nitrogen atoms near the mesopause below; special circumstances such as solar flares producing more than 10^6 photons $cm^{-2}sec^{-1}$ can lead to an unusual liberation of nitrogen atoms.

4.2. Effects of Charge Transfers

There is the possibility that dissociative recombination is not operative for nitrogen, if the following processes of charge transfer are considered

$$N_2^+ + O \rightarrow N_2 + O^+ \qquad (.72a)$$

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ \qquad (.72b)$$

$$O^+ + O_2 \rightarrow O + O_2^+ \qquad (.72c)$$

for which a rate coefficient β_O or β_{O_2} could be great enough to counterbalance a direct dissociation recombination process (.70). Considering the E layer where the electronic concentration is of the order of 10^5 cm^{-3}, $\beta_O n(O)$ or $\beta_{O_2} n(O_2)$ should be greater than $10^{-2}sec^{-1}$, namely

$$\beta_O > 10^{-14}\ cm^3 sec^{-1} \qquad (.73)$$

Such a process has been considered as completely operative by Harteck[32] who neglects process (.70); which would not occur in the upper atmosphere where the charge exchange reaction will occur before. In fact, in the F region where the electronic concentration is of the order of $10^6 cm^{-3}$ and the concentration of atomic oxygen not greater than 10^9, the rate coefficient β_O of the charge transfer should be more than 10^{-10} cm^3sec^{-1} unless the high value of the dissociation recombination is wrong by several orders of magnitude. In any case, a rate coefficient of 10^{-10} $cm^3 sec^{-1}$ at thermospheric temperatures would require a charge exchange cross section larger than $10^{-16} cm^2$ which is too high for the low energies involved.

4.3. Effects of Ion-Atom Interchange Collision

Bates[40] has shown that an alternative mechanism to charge transfer, which is extremely inefficient at thermospheric temperatures, must be considered. It is the exothermic ion-atom interchange

$$X^+ + YZ \longrightarrow XY^+ + Z \qquad (.74)$$

which can be compared to the two-body chemical processes and, therefore, may have a cross section not too different from the kinetic cross section. In other words, the rate coefficient could, without difficulty, be as high as 10^{-10} $cm^3 sec^{-1}$. The rate of various gaseous reactions according to (.74) has been studied experimentally by Stevenson and Schissler[41,42] and values are obtained in the range $10^{-9} cm^3 sec^{-1}$ to $10^{-10} cm^3 sec^{-1}$. Furthermore, Potter[43] has determined $10^{-8} cm^3 sec^{-1}$ for $O^+ + N_2 \longrightarrow NO^+ + N$.

In any case, it can be concluded that the ion-atom interchange process is an alternative process to the charge exchange and is more efficient in the thermosphere. Therefore, the following processes must be dominant

$$O^+ + O_2 \longrightarrow O_2^+ + O + 1.5 \text{ eV} \qquad (.75)$$

$$O^+ + N_2 \longrightarrow NO^+ + N + 1 \text{ eV} \qquad (.76)$$

for which the rate coefficients will be denoted by α_{O_2} and α_{N_2}, respectively. As far as the molecular nitrogen ion is concerned the reaction is

$$N_2^+ + O \longrightarrow NO^+ + N \qquad (.77)$$

with a rate coefficient α_O which may be very great.

These ion-atom interchanges in the ionosphere should be followed by dissociative recombinations

$$O_2^+ + e \longrightarrow O + O \qquad (.78)$$

for which we assume a coefficient $\alpha_{O_2} = 3 \times 10^{-8} cm^3 sec^{-1}$ and

$$NO^+ + e \longrightarrow N + O \qquad (.79)$$

for which the dissociation recombination coefficient is not known.

However, Harteck and Dondes [44] considered that dissociation recombination is effective only to an extent of 15 °/∘ ± 5°/∘ and that the most important process must be

$$NO^+ + e \longrightarrow NO + h\nu \qquad (.80)$$

If the radiative recombination takes place, the recombination process cannot be sufficiently rapid and it should be considered that nitric oxide ions have a very long life time. The ion-molecule interchange process should play the most important role.

4.4. Ionospheric Production of Nitric Oxide and Atomic Nitrogen

When nitric oxide ions are produced in the ionosphere by ion-atom interchange collisions, the aeronomic problem appears to be different to that in chemical equilibrium. Unfortunately, it can be seen from a summary of the salient features of the reactions represented by (.70) to (.80) that there are no numerical data available for the parameters involved.

For example, it would be permissable to claim that there is no production of nitric oxide and atomic nitrogen if the charge exchange process (.72b) is the only loss process for molecular nitrogen ions. On the other hand, if the ion-molecule interchange collisions (.76) and (.77) were assumed to be the mechanism of disappearance of ions, it could be concluded that almost the entire ionization would finally lead to nitric oxide and atomic nitrogen in the upper ionosphere. Furthermore, if (.79) were negligible compared to (.80), there would be a continuous increase of nitric oxide.

Since the possible errors in the determinations of products of charge transfer (to be neglected) and ion-atom interchange (to be taken into account) are too large, it is unwise at this time to place much emphasis on numerical data. It should be pointed out that a great deal more work will be required before any mechanism can be proposed, with confidence, for the ionic recombination in the ionosphere. For this reason the following analyses must be considered as exploratory possibilities for the production of nitrogen atoms and nitric oxides molecules.

Let us group the various ionospheric processes as follows :

$$\left\{\begin{array}{ll} N_2^+ + e \longrightarrow N + N & (.70) \\ N_2^+ + O \longrightarrow NO^+ + N \text{ (fraction X of the entire process)} & (.77) \end{array}\right.$$

$$\left\{\begin{array}{ll} O^+ + O_2 \longrightarrow O_2^+ + O & (.75) \\ O^+ + N_2 \longrightarrow NO^+ + N \text{ (fraction Y of the entire process)} & (.76) \end{array}\right.$$

$$\left\{\begin{array}{ll} NO^+ + e \longrightarrow N + O & (.78) \\ NO^+ + e \longrightarrow NO + h\nu \text{ (fraction Z of the entire process)} & (.79) \end{array}\right.$$

and

$$\left\{\begin{array}{ll} N + NO \longrightarrow N_2 + O & (.43) \\ N + O_2 \longrightarrow NO + O & (.46) \end{array}\right.$$

The photoionization processes are represented by

$$N_2 + h\nu \longrightarrow N_2^+ + e \qquad (.81)$$

$$O + h\nu \longrightarrow O^+ + e \qquad (.82)$$

$$NO + h\nu \longrightarrow NO^+ + e \qquad (.59)$$

for which the respective ionization rate coefficients are I_{N_2}, I_O and I_{NO}.

Considering ionization equilibria and the effect of photodissociation, the following equations can be written by using the complete set of equations :

$$n(N)\ \left[b_6\, n(NO) + b_7\, N(O_2) \right] =$$

$$n(N_2)\ \left[2J_{N_2} + I_{N_2}(2-XZ) \right] + n(O)\ I_O Y(2-Z)$$

$$+\, n(NO)\ \left[J_{NO} + (1-Z) I_{NO} \right] \qquad (.83)$$

$$n(NO)\ \left[J_{NO} + b_6\, N(N) \right] = Z \left[Xn(N_2) I_{N_2} + Yn(O)\ I_O \right.$$

$$\left. +\, n(NO)\ I_{NO} \right] + b_7 n(O_2)\ n(N) \qquad (.84)$$

The addition of (.83) and (.84) leads to the general equation

$$n(N_2)\ \left[J_{N_2} + I_{N_2} \right] + n(O)\ I_O\, Y = b_6\, n(NO) n(N) \qquad (.85)$$

Simple expressions for atomic nitrogen and nitric oxide concentrations are obtained when photodissociation is neglected compared to ionization and when the radiative recombination of NO^+ is neglected compared to dissociative recombination. Thus the equilibrium concentrations of N and NO are

$$n(N) = \frac{n(N_2) I_{N_2} + Y\, n(O)\ I_O}{b_7\ n(O_2)} \qquad (.86)$$

and

$$n(NO) = \frac{b_7 n(O_2)}{b_6} \qquad (.87)$$

with, therefore,

$$n(N_2) I_{N_2} + Y\, n(O)\ I_O = b_6\, n(N)\ \ n(O) \qquad (.88)$$

Consequently, the concentration of nitric oxide depends only on the concentration of molecular oxygen, and atomic nitrogen is related to the ionization of molecular nitrogen and may be associated with the ionization of atomic oxygen.

4.5. Atomic Nitrogen and Nitric Oxide Conditions in the Ionosphere

The problem of the vertical distribution of nitric oxide in the thermosphere is solved if there are enough nitrogen atoms. Equation (.87) gives the values of the concentration and figure 6 gives the ratio $n(NO)/n(O_2)$ for various temperatures. It is clear that nitric oxide is a minor constituent since its concentration is a small fraction of the concentration of molecular oxygen.

Byram, Chubb and Friedman [45] measured the concentration of molecular oxygen up to 180 km, where it is $4 \times 10^8 cm^{-3}$. A temperature of 1000° K leads to an NO concentration of the order of 2×10^5 cm^{-3}. The same concentration is obtained if a concentration of 10^8 oxygen molecules corresponds to a temperature of about 2000° K. At low altitudes, where the temperature is of the order of 300° K, $n(NO)/n(O_2) = 3 \times 10^{-6}$ and therefore even 3×10^{11} oxygen molecules cannot lead to a concentration of nitric oxide greater than $10^6 cm^{-3}$.

In order to determine the concentration of atomic nitrogen, it is necessary to know the ionization rate of molecular nitrogen and atomic oxygen in the whole thermosphere. In fact, an exact determination of the vertical distribution of atomic nitrogen requires the knowledge of $n(N_2)$, $n(O)$ and $n(O_2)$, as well as the temperature. Furthermore, it is necessary to know the number of ultraviolet photons available for ionization of N_2 and O, and the rate of ionization by X-rays. For example, if we consider ionization by X-rays of about 50 A with an energy of 0.1 erg $cm^{-2}sec^{-1}$, the number of resulting nitrogen atoms at 100 km is of the order of 3.5×10^6 cm^{-3}, i.e. the concentration deduced from the predissociation process (see Table I). Therefore, atomic nitrogen is a minor constituent in the lower thermosphere.

In order to show the maximum possibilities let us take a production rate of 2000 nitrogen atoms $cm^{-3}sec^{-1}$ in the E and F_1

layers with respective scale heights of 10 km and 50 km corresponding to about 4×10^8 photons $cm^{-2}sec^{-1}$ and 2×10^9 photons $cm^{-2}sec^{-1}$. The following results are obtained :

Temperature (°K)	$n(N)n(O_2)$ (cm^{-6})	$n(O_2)$ (cm^{-3})	$n(N)$ (cm^{-3})
300	2.5×10^{19}	2.5×10^{11}	10^8
500	3×10^{17}	10^9	3×10^8
750	3×10^{16}	10^9	3×10^7
1000	10^{16}	10^9	10^7

The maximum value of the atomic nitrogen concentration would be obtained in the F_1 layer and it would be of the same order as $n(O_2)$ between 150 km and 180 km if the temperatures were sufficiently low. However, steady conditions cannot be assured for atomic nitrogen in the whole thermosphere, since the life time of a nitrogen atom varies with height. The life time τ_N defined by

$$\tau_N = \frac{0.7}{2\, b_7 n(O_2)} \qquad (.89)$$

are shown in Figure 7. In the E layer where the temperature is low, there may be some variation, but conditions are such that there is no great difference between day and night. But in the F_1 layer, where there is a photoequilibrium, the life time of a nitrogen atom may be shorter than one night and, therefore, there is a daily variation. As far as the F_2 layer is concerned, life times become sufficiently long to allow an effective action of diffusion. Since the absolute concentration will vary according to the varying boundary conditions in the F_1 layer, the concentration of atomic nitrogen cannot remain constant in the upper levels of the thermosphere. Furthermore, n(N) will be subject to variations associated with solar activity.

References

1. Chapman, S., The Photochemistry of Atmospheric Oxygen, Rep. on Progress in Physics, 9, 92, 1943.
2. Nicolet, M., Dynamic Effects in the High Atmosphere, Chapter 13 in The Earth as a Planet, Ed. G.P. Kuiper, University of Chicago Press, 1954.
3. Herzberg, G., The Spectra of Diatomic Molecules, 2nd Ed. D. Van Nostrand, New York, 1956.
4. Vigroux, E., Contributions à l'étude expérimentale de l'absorption de l'ozone, Annales Phys. (12), 8, 1, 1953.
5. Bates, D.R. and Nicolet, M., the Photochemistry of the Atmospheric Water Vapor, J. Geophys. Res., 55, 301, 1950.
6. Nicolet, M. and Mange, P., The Dissociation of Oxygen in the High Atmosphere, J. Geophys. Res., 59, 16, 1954
7. Berg, O.E., Koomen, M., Meredith, L., Scolnik, R., The Altitude of the (OI) 5577A Line in the Night Airglow Measured from a Rocket, J. Geophys. Res., 61, 302, 1956.
8. Koomen, M., Scolnik, R. and Tousey, R., Distribution of the Night Airglow (OI) 5577A and Na D Layers Measured from a Rocket, J. Geophys. Res., 61, 304, 1956.
9. Heppner, J. P. and Meredith, L.H., Nightglow Emission Altitudes from Rocket Measurements, J. Geophys. Res., 63, 51, 1958.
10. Bates, D.R., Some Reactions Occurring in the Earth's Upper Atmosphere, Annales Geophys., 8, 194, 1952.
11. Bates, D.R., The Physics of the Upper Atmosphere, Chapter 12 in the Earth as a Planet, Ed. G.P. Kuiper, University of Chicago Press, 1954.
12. Nicolet, M., The Aeronomic Problem of Nitrogen Oxides, J. Atm. Terr. Phys., 7, 152, 1955.
13. Nicolet, M., Contribution à l'étude de la structure de l'ionosphère, Inst. Roy. Météor., Mémoires Vol. 19, 162 pages, 1945.
14. The Rocket Panel, Phys. Rev., 88, 1027, 1952.

15. Johnson, F.S., Temperature Distribution of the Ionosphere under Control of Thermal Conductivity, J. Geophys. Res., 61, 71, 1956.

16. Kallmann, H.K., White, W.B. and Newell, Jr, H.E., Physical Properties of the Atmosphere from 90 to 300 Kilometers, J. Geophys. Res., 61, 513, 1956.

17. Herzberg, G. and Herzberg, L., Production of Nitrogen Atoms in the Upper Atmosphere, Nature, 161, 283, 1948.

18. Bialecke, E.P. and Dougal, A.A., Pressure and Temperature Variation of the Electron-Ion Recombination Coefficient in Nitrogen, J. Geophys. Res., 63, 539, 1958.

19. Waifan, N., Walker, W.C. and Weiseler, G.L., Photoionization Efficiencies and Cross Sections in O_2, N_2, CO_2, A, H_2O, N_2 and CH_4, Phys. Rev., 99, 542, 1955.

20. Curtiss, J.P., Absorption Coefficients of Air and Nitrogen for the Extreme Ultraviolet, Phys. Res., 94, 908, 1954.

21. Astoin, N. and Granier, J., Sur le spectre d'absorption de l'azote dans l'ultraviolet extrême, Comptes Rendus Acad. Sc., Paris, 244, 1350, 1957.

22. Byram, E.T., Chubb, T.A. and Friedman, H , The Solar X-ray Spectrum and the Density of the Upper Atmosphere, J. Geophys. Res 61, 251, 1956.

23. Chubb, T.A., Friedman, H., Kreplin, R.W. and Kupperian, Jr., J.E., Lyman Alpha and X-ray Emissions During a Small Solar Flare, J. Geophys. Res., 62, 389, 1957.

24. Neuberger, D. and Duncan, A.B.F., Fluorescence of Nitrogen Dioxide, J. Chem. Phys., 22, 1693, 1954.

25. Hall, T.C. and Blacet, F.E., Separation of the Absorption Spectra of NO_2 and N_2O_4 in the Range of 2400-5000 A, J. Chem. Phys., 20, 1745, 1952.

26. Kaufman, F., Air Afterglow and Kinetics of Some Reactions of Atomic Oxygen, J. Chem. Phys., 28, 352, 1958.

27. Kaufman, F., Gerri, N.J. and Bowman, R.E., Role of Nitric Oxide in the Thermal Decomposition of Nitrous Oxide, J. Chem. Phys., 25, 106, 1956.

28. Ford, H.W. and Endow, N., Rate Constant at Low Concentrations III. Atomic Oxygen Reactions in the photolysis of Nitrogen Dioxide at 3660 A, J. Chem. Phys., 27, 1156, 1957.

29. Kistiakowsky, G.B., and Volpi, C.G., Reactions of Nitrogen Atoms. I. Oxygen and Oxides of Nitrogen, J. Chem. Phys., 27, 1141, 1957.

30. Spealman, M.L. and Rodebush, W.H., The Reactions of Some Oxides of Nitrogen with Atomic Oxygen and Nitrogen, J. Amer. Chem. Soc., 57, 1474, 1935.

31. Johnston, H.S. and Crossby, H.J., Kinetics of the Fast Gas Reaction between Ozone and Nitric Oxide, J. Chem. Phys., 22, 689, 1954.

32. Harteck, P., A Discussion on the Reactions of Nitrogen and Nitrogen Oxides in the Upper Atmosphere, in Proc. Conf. Chemical Aeronomy, Ed. M. Zelikoff, Pergamon Press, London, p. 32, 1957.

33. Glick, H.S., Klein, J.J. and Squire, W., Single-Pulse Shock Tube Studies of the Kinetics of the Reaction $N_2 + O_2 \rightleftharpoons 2NO$ between 2000-3000°K, J. Chem. Phys., 27, 850, 1957.

34. Kistiakowsky, G.B. and Volpi, G.G., Reactions of Nitrogen Atoms, J. Chem. Phys. 28, 665, 1958.

35. Vetter, K., Kinetic der thermischen Zersetzung und Bildung von Stickoxyd, Zeit. Elektrochemie und Angew. Physik. Chemie, 53, 369, 1949.

36. Wise, H. and Trech, M.F., Kinetics of Decomposition of Nitric Oxide at Elevated Temperatures, J. Chem. Phys., 20, 22 and 1724, 1952.

37. Kaufman, F. and Kelso, J.R., Thermal Decomposition of Nitric Oxide, J. Chem. Phys., 23, 1702, 1955.

38. Friedman, H., Photoelectric Measurements of Solar X-Rays and Ultraviolet Radiation, Rapport Commission Etudes Relations Phénomènes Solaires et Terrestres, 9, 41, 1957.

39. Bates, D.R., The Emission of the Negative System of Nitrogen from the Upper Atmosphere and the Significance of the Twilight Flash in the Theory of the Ionosphere, Proc. Roy. Soc. London, A 196, 562, 1959.

40. Bates, D.R., Charge Transfer and Ion-Atom Interchange Collisions, Proc. Phys. Soc. A 68, 344, 1955.

41. Stevenson, D.P. and Schissler, D.O., Rate of the Gaseous Reactions $X^+ + YH = XH^+ + Y$, J. Chem. Phys., 23, 1353, 1955.

42. Schissler, D.O. and Stevenson, D.P., Reactions of Gaseous Molecular Ions with Gaseous Molecules, J. Chem. Phys., 24, 926, 1956.

43. Potter, R.F., Ion-Atom Interchange in Air, J. Chem. Phys. 23, 2462, 1956.

44. Harteck, P. and Dondes, S., Decomposition of Nitrogen Oxide and Nitrogen Dioxide by the Impact of Fission Fragment of Uranium - 235, J. Chem. Phys., 27, 546, 1957.

45. Byram, E.T., Chubb, T.A. and Friedman, H., The Dissociation of Oxygen at High Altitudes, p. 211 in the Proceedings of the Conference on Chemical Aeronomy, The Threshold of Space, Ed. M. Zelikoff, Pergamon Press, London, 1957.

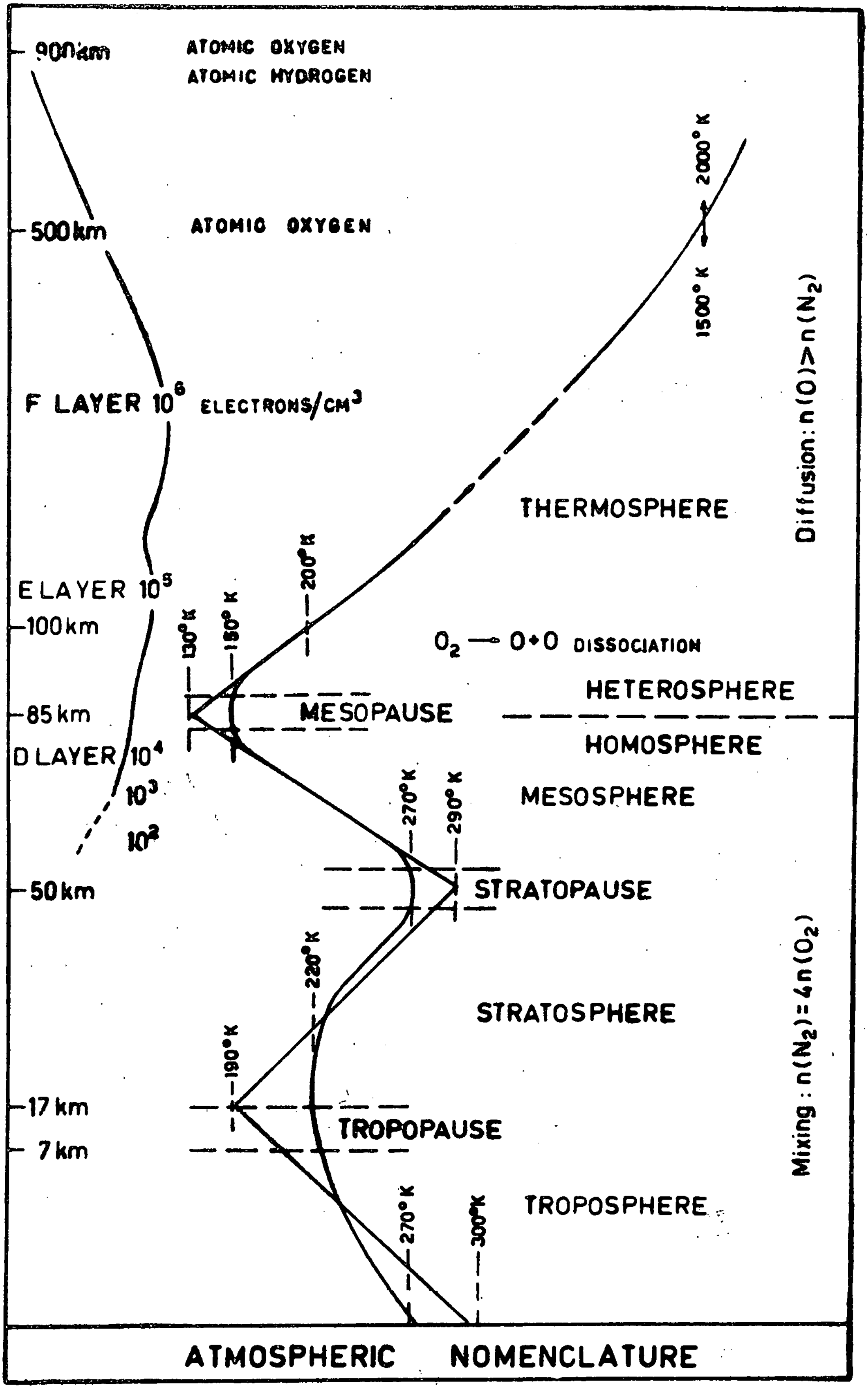
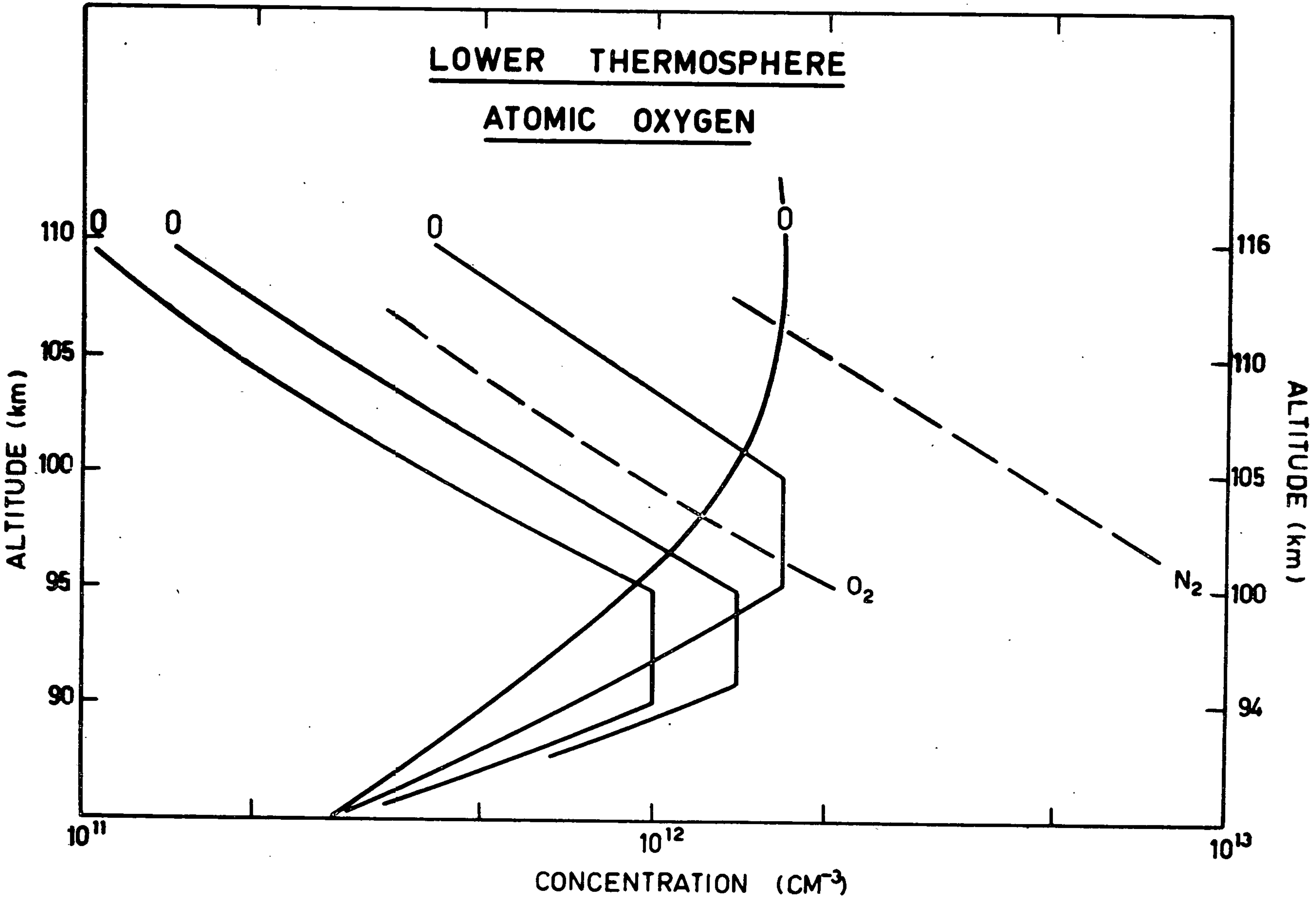

900 km
ATOMIC OXYGEN
ATOMIC HYDROGEN
2000° K
500 km
ATOMIC OXYGEN
1500° K
Diffusion: n(O) > n(N2)
F LAYER 10^6 ELECTRONS/CM^3
THERMOSPHERE
E LAYER 10^5
200° K
130° K
150° K
100 km
O2 → O+O DISSOCIATION
HETEROSPHERE
85 km
MESOPAUSE
HOMOSPHERE
D LAYER 10^4
10^3
10^2
270° K
290° K
MESOSPHERE
50 km
STRATOPAUSE
220° K
STRATOSPHERE
Mixing: n(N2) = 4n(O2)
190° K
17 km
TROPOPAUSE
7 km
270° K
300° K
TROPOSPHERE
ATMOSPHERIC NOMENCLATURE

Figure 1.



LOWER THERMOSPHERE
ATOMIC OXYGEN
O
O
O
O
O_2
N_2
ALTITUDE (km)
110
105
100
95
90
ALTITUDE (km)
116
110
105
100
94
10^{11}
10^{12}
10^{13}
CONCENTRATION (CM^{-3})

Figure 2

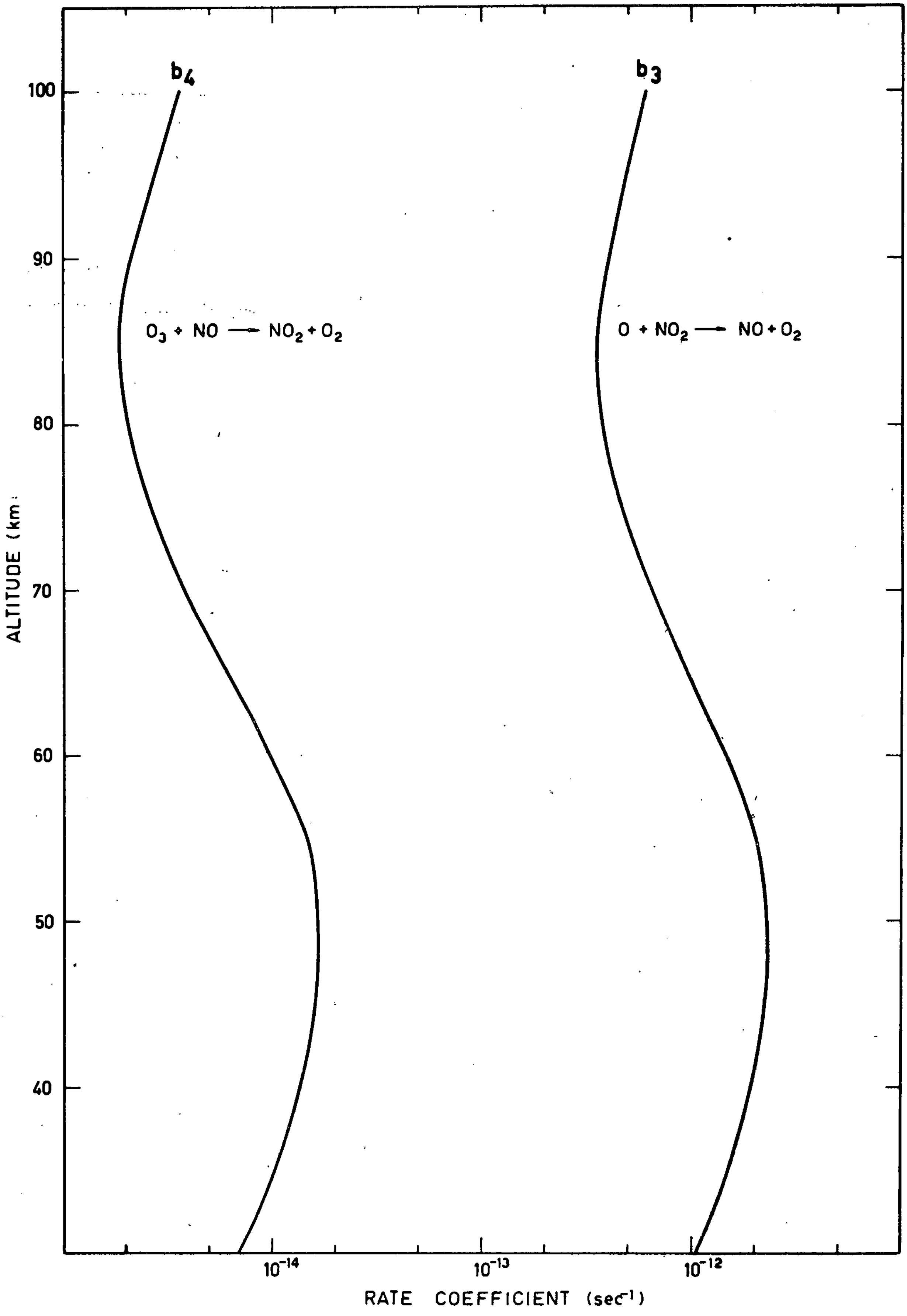

b4
b3
$O_3 + NO \longrightarrow NO_2 + O_2$
$O + NO_2 \longrightarrow NO + O_2$
ALTITUDE (km)
100
90
80
70
60
50
40
10^{-14}
10^{-13}
10^{-12}
RATE COEFFICIENT (sec^{-1})

Figure 3

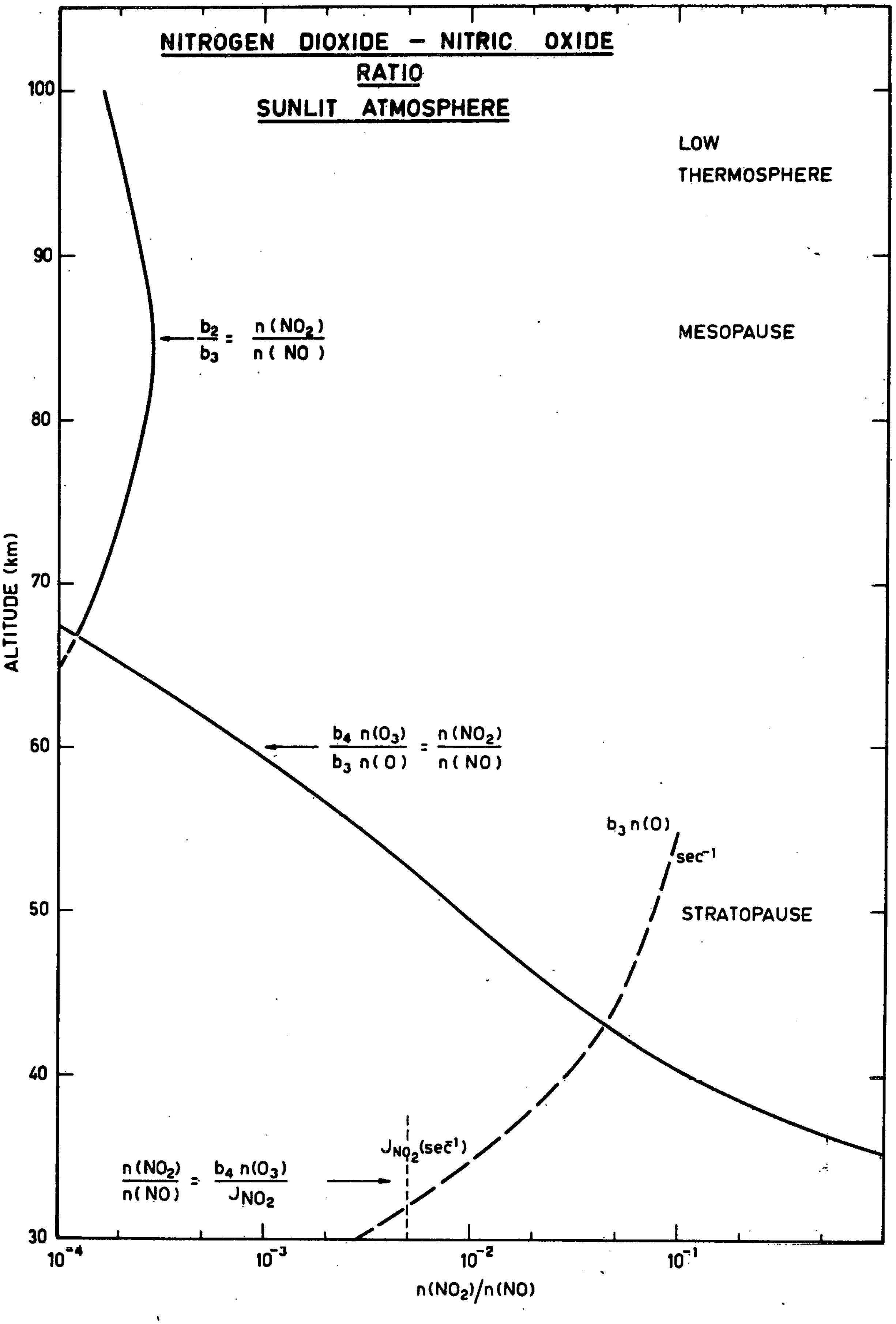

NITROGEN DIOXIDE – NITRIC OXIDE RATIO
SUNLIT ATMOSPHERE
LOW THERMOSPHERE
MESOPAUSE
STRATOPAUSE
$\frac{b_2}{b_3} = \frac{n(NO_2)}{n(NO)}$
$\frac{b_4\, n(O_3)}{b_3\, n(O)} = \frac{n(NO_2)}{n(NO)}$
$b_3\, n(O)$ sec^{-1}
$J_{NO_2}(sec^{-1})$
$\frac{n(NO_2)}{n(NO)} = \frac{b_4\, n(O_3)}{J_{NO_2}}$
ALTITUDE (km)
100
90
80
70
60
50
40
30
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$n(NO_2)/n(NO)$

Figure 4

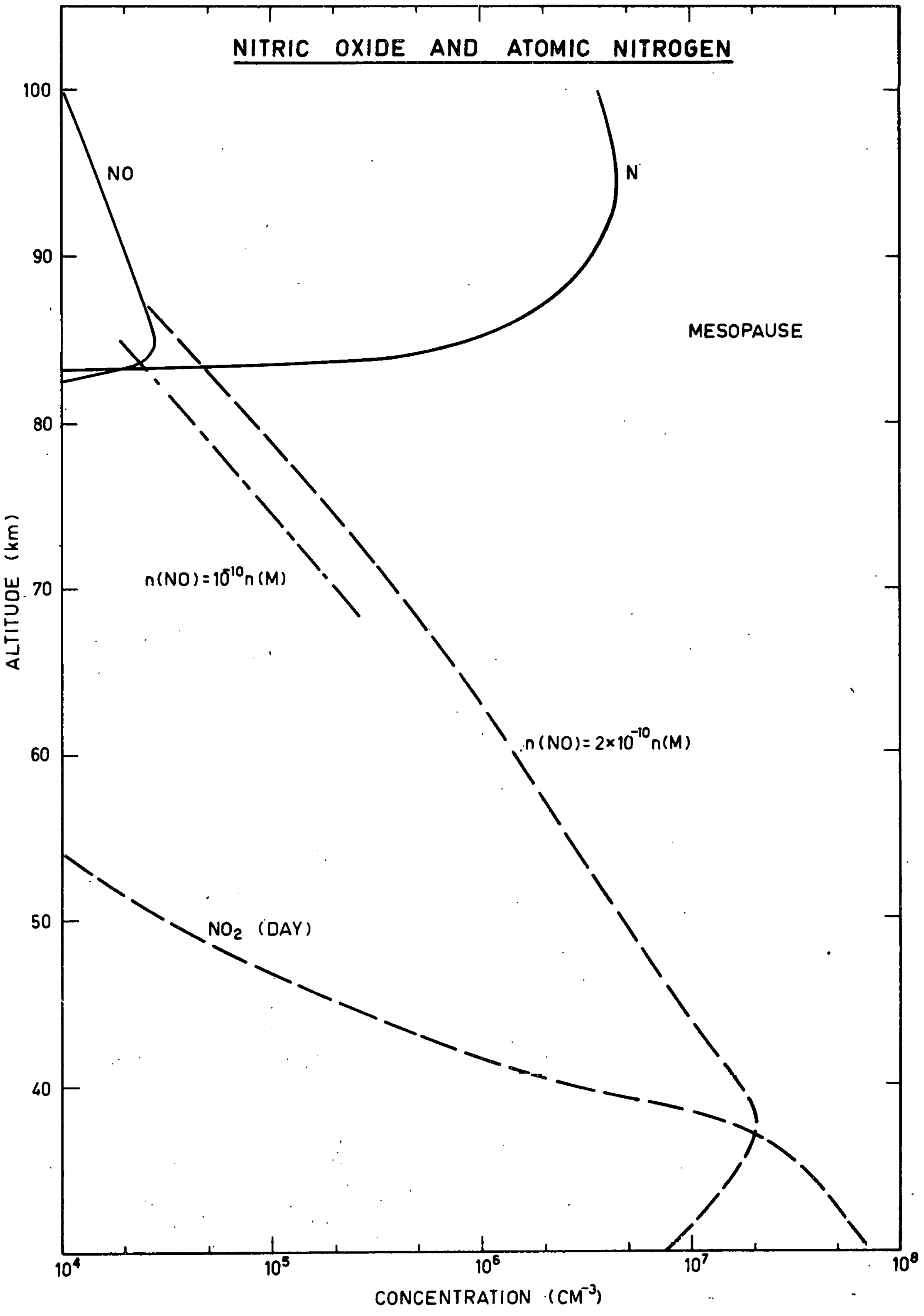

NITRIC OXIDE AND ATOMIC NITROGEN
NO
N
MESOPAUSE
n(NO) = 10⁻¹⁰ n(M)
n(NO) = 2×10⁻¹⁰ n(M)
NO2 (DAY)
ALTITUDE (km)
100
90
80
70
60
50
40
10^4
10^5
10^6
10^7
10^8
CONCENTRATION (CM^-3)

Figure 5

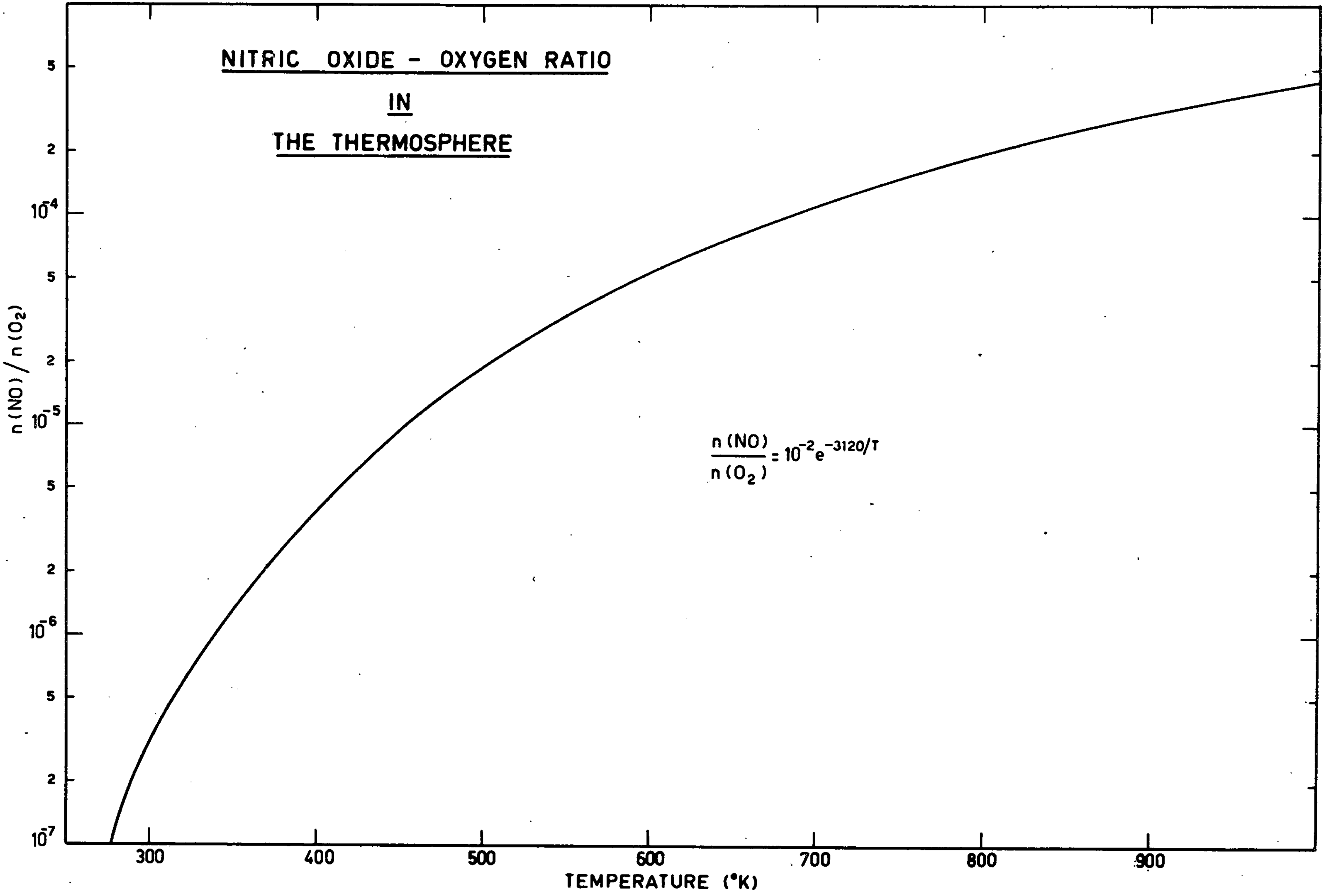

NITRIC OXIDE - OXYGEN RATIO
IN
THE THERMOSPHERE
n (NO) / n (O$_2$)
$\frac{n(NO)}{n(O_2)} = 10^{-2} e^{-3120/T}$
5
2
10^{-4}
5
2
10^{-5}
5
2
10^{-6}
5
2
10^{7}
300
400
500
600
700
800
900
TEMPERATURE (°K)

Figure 6

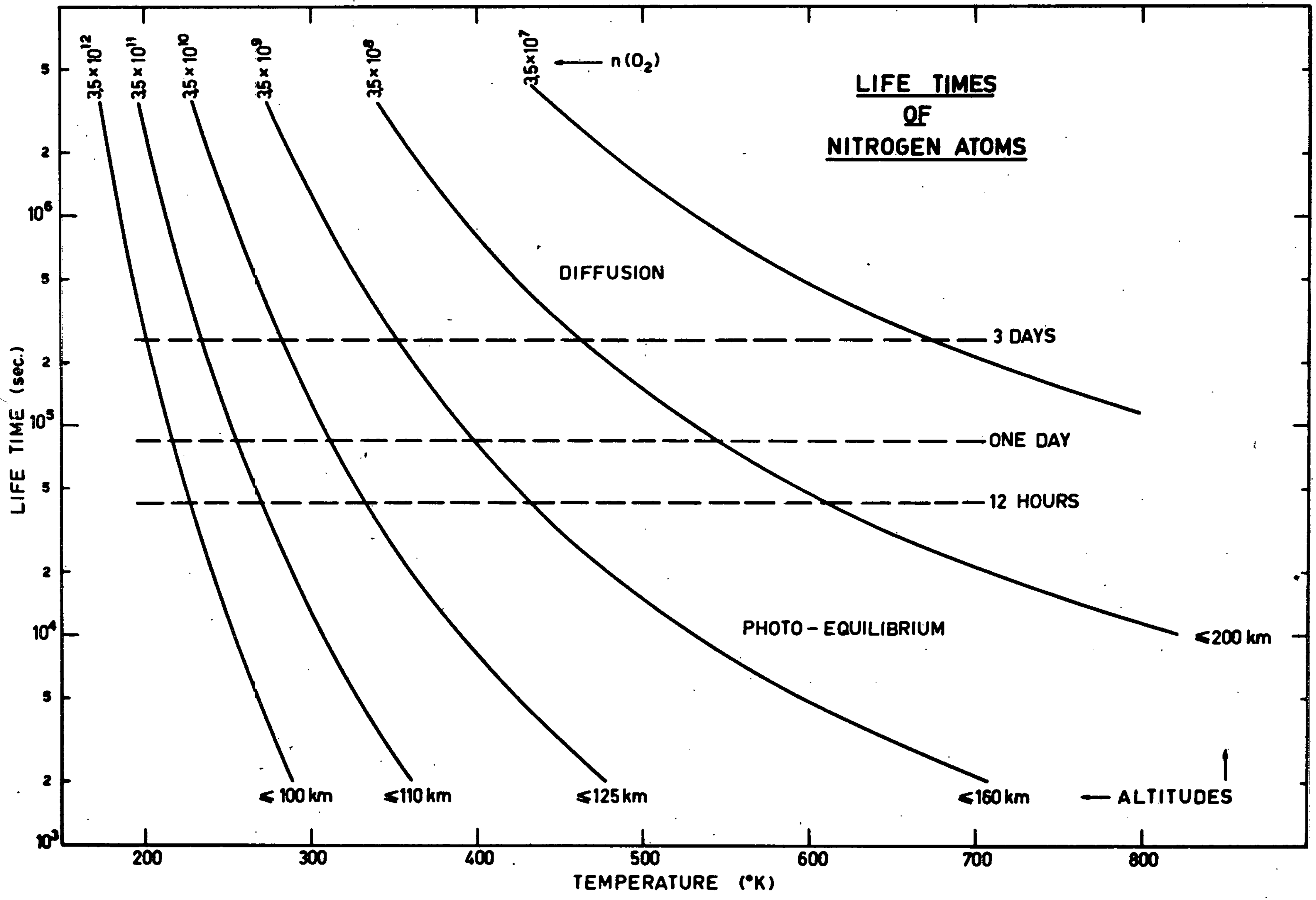

LIFE TIMES OF NITROGEN ATOMS
LIFE TIME (sec.)
TEMPERATURE (°K)
3,5 × 10^12
3,5 × 10^11
3,5 × 10^10
3,5 × 10^9
3,5 × 10^8
3,5 × 10^7
n(O2)
DIFFUSION
PHOTO - EQUILIBRIUM
3 DAYS
ONE DAY
12 HOURS
≤ 100 km
≤ 110 km
≤ 125 km
≤ 160 km
≤ 200 km
ALTITUDES
10^3
2
5
10^4
2
5
10^5
2
5
10^6
2
5
200
300
400
500
600
700
800

Figure 7