

INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE

3 - Avenue Circulaire

B - 1180 BRUXELLES

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The origin of Nitric oxide in the terrestrial atmosphere  
by M. NICOLET

BELGISCH INSTITUUT VOOR RUIMTE-AERONOMIE

3 - Ringlaan

B - 1180 BRUSSEL

#### FOREWORD

The Note entitled "The origin of nitric oxide in the terrestrial atmosphere" will be published in Planetary and Space Science.

#### AVANT-PROPOS

L'article intitulé "The origin of nitric oxide in the terrestrial atmosphere" a été présenté comme "Research Note" qui sera publiée dans Planetary and Space Science.

#### VOORWOORD

Dit werk, "The origin of nitric oxide in the terrestrial atmosphere" zal verschijnen in Planetary and Space Science.

#### VORWORT

Die Arbeit "The origin of nitric oxide in the terrestrial atmosphere" wird als "Research Note" in Planetary and Space Science herausgegeben werden.

# THE ORIGIN OF NITRIC OXIDE IN THE TERRESTRIAL ATMOSPHERE

by

M. NICOLET.

## Abstract

Nitric oxide in the mesosphere and stratosphere is due to a downward transport from the thermosphere above the E layer where it is formed by a reaction of molecular oxygen with normal and excited nitrogen atoms produced by dissociative recombination of ionospheric ions.

## Résumé

On démontre que la présence de l'oxyde d'azote dans la mésosphère et dans la stratosphère résulte du transport à partir de la thermosphère de cette molécule. Celle-ci est formée surtout au-dessus de la région E ionosphérique par une réaction de la molécule d'oxygène avec des atomes d'azote, non seulement à l'état normal, mais également dans l'état excité, qui sont produits au cours de la recombinaison dissociative des ions ionosphériques.

## Samenvatting

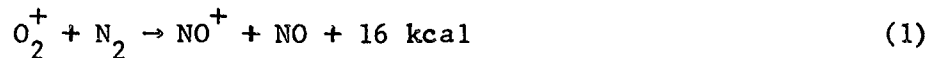
Stikstofoxyde wordt gevormd in de thermosfeer, boven de E-laag, door een reactie van moleculaire zuurstof met normale en aangeslagen stikstofatomen, die ontstaan door dissociatieve recombinitie met ionosferische ionen. Door een neerwaartse verplaatsing komt ze in de mesosfeer en stratosfeer terecht.

## Zusammenfassung

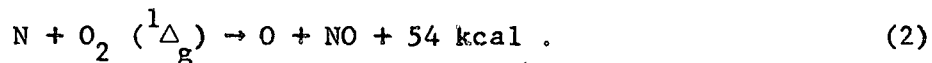
Die Anwesenheit von NO in der Mesosphäre und in der Stratosphäre ergibt sich aus einer Wegbringung dieser Moleküle aus der Thermosphäre. Das Stickstoffoxyd wird meistens auf der obern Seite der ionosphärischen E-Schichte durch eine Reaktion zwischen Molekularsauerstoff und normalen sowie angeregten Stickstoffatomen, die aus dissoziativen Rekombinationen der ionosphärischen Ionen folgen, gebildet.

Recent observations in the upper mesosphere and lower thermosphere [Barth, 1964, 1966 ; Pearce, 1969] and in the upper stratosphere and lower mesosphere [Pontano and Hale, 1969] indicate that nitric oxide is present in significant amount even though its local production seems to be very small [Nicolet, 1945, 1955, 1965a, b ; Bates, 1952, 1954 ; Nicolet and Aikin, 1960 ; Barth, 1961].

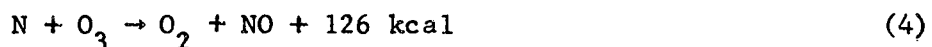
In order to increase the source of nitric oxide in the lower thermosphere, Nicolet [1965b] suggested the possibility of an indirect way of production by the following reaction



with a very low rate coefficient since a double-bond breakage is required. However, such a reaction has not been observed in the laboratory [Ferguson, 1967], and the rate coefficient is less than  $10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  at several hundred degrees. Hunten and McElroy [1968] after rejecting the preceding reaction proposed as an alternative reaction



This cannot be accepted as the source since the free nitrogen atoms are involved in normal aeronomic processes such as



and since it is not supported by experimental data [Clark and Wayne, 1969 ;

Findlay et al, 1969]. The rate coefficient of (2), which is of the order of  $2 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  at  $200^\circ\text{K}$ , shows clearly that the analysis by Hunt~~en~~ and McElroy cannot be considered as the solution to the puzzling question of the source of nitric oxide.

We suggest, that the nitric oxide in the mesosphere and stratosphere is due to a downward transport from the thermosphere above the E layer where it is produced.

On the various aeronomic processes leading to the union of odd nitrogen atoms, only the following reaction [Bates, 1952 ; Nicolet, 1965a] is important :



with a rate coefficient

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

which may represent the laboratory measurements [Philipps and Schiff, 1962 ; Schiff, 1969].

Denoting by  $b_7$  the appropriate rate coefficient of the most important process among the reactions (2), (3), (4) and (5), we have that in chemical equilibrium

$$n(\text{NO}) = \frac{b_7 n_7}{b_6} \quad (7a)$$

where the  $n$  indicates the particle concentration with the equation number as an identifying subscript. At altitudes above the E layer, the expression

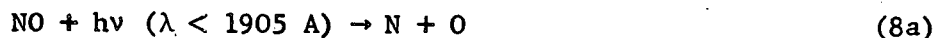
$$b_7 n(\text{O}_2) = 5 \times 10^{-13} T^{1/2} e^{-3500/T} n(\text{O}_2) \text{ sec}^{-1} \quad (7b)$$

can be adopted in using all recent laboratory determinations [Wilson, 1967 ; Vlastaras and Winkler, 1967]. Thus,

$$n_*(\text{NO}) = 3 \times 10^{-1} e^{-3500/T} n(\text{O}_2) \text{ cm}^{-3} \quad (7c)$$

is the chemical equilibrium value of the nitric oxide concentration in the thermosphere.

In addition to the nitric oxide loss process (6) which occurs during the day and night, account must be taken of photodissociation [Bates, 1952, 1954]. The photodissociation process



corresponds to a predissociation observed in the  $\gamma$ ,  $\beta$ ,  $\delta$  and  $\epsilon$  bands [see Heicklen and Cohen, 1968]. With a transition probability of about  $2 \times 10^7 \text{ sec}^{-1}$  [Callear and Smith, 1964], the photodissociation coefficient at zero optical depth, i.e. in the whole thermosphere, is

$$J_{\text{NO}} = 5 \times 10^{-6} \text{ sec}^{-1} \quad (8b)$$

With (6), (7) and (8) we have that in photochemical equilibrium in the thermosphere

$$\frac{n(\text{NO})}{n(\text{N})} = \frac{b_7 n(\text{O}_2)}{J_{\text{NO}} + b_6 n(\text{N})} \quad (9a)$$

Chemical equilibrium for nitric oxide prevails provided the concentration of atomic nitrogen is not less than  $10^6 \text{ cm}^{-3}$ .

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

$$\frac{dn(N)}{dt} + n(N) [b_6 n(NO) + b_7 n_7] = n(NO) J_{NO} + 2 P(N_2) \quad (10)$$

in which the last term on the right takes into account the nitrogen production by photodissociation and photoionization processes. Above the E layer, atomic nitrogen may reach conditions not far from photochemical equilibrium conditions since  $b_7 n(O_2)$  is always greater than  $3 \times 10^{-5} \text{ sec}^{-1}$ . In the lower thermosphere, where the temperature is low, photochemical equilibrium exists only if  $n(NO)$  is greater than the chemical equilibrium concentration. In the mesosphere, the life time of a nitrogen atom is short due to the special effect of (5).

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

$$\frac{dn(NO)}{dt} + n(NO) [J_{NO} + b_6 n(N)] = b_7 n_7 n(N) + P(NO) \quad (11)$$

in which  $P(NO)$  is an independent source of nitric oxide to be identified. Since photodissociation is a slow process, equilibrium conditions can be reached only if  $n(N)$  is not less than  $5 \times 10^6 \text{ cm}^{-3}$ . This cannot happen in the mesosphere ; in the thermosphere, an important production of nitrogen atoms is required.

The general photochemical conditions which must be applied to NO and N are, from (10) and (11),

$$\frac{dn(N)}{dt} + \frac{dn(NO)}{dt} + 2 b_6 n(NO) n(N) = 2 P(N_2) + P(NO) . \quad (12)$$

Atomic nitrogen is produced by a predissociation process [Herzberg and Herzberg, 1948 ; Bates, 1954] with a rate coefficient for zero optical depth

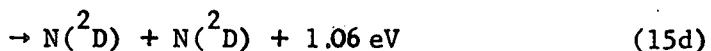
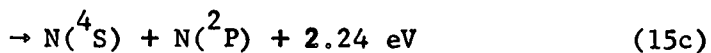
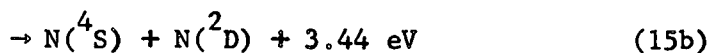
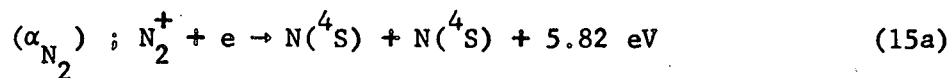
$$J_{N_2} = 5 \times 10^{-14} \text{ sec}^{-1} \quad (13)$$

which leads to a production of about 40 nitrogen atoms  $\text{cm}^{-3} \text{ sec}^{-1}$  at 100 km and only 1 atom  $\text{cm}^{-3} \text{ sec}^{-1}$  at the mesopause. Dissociative ionization occurs in the mesosphere but its effect is extremely small, less than 1 atom  $\text{cm}^{-3} \text{ sec}^{-1}$ .

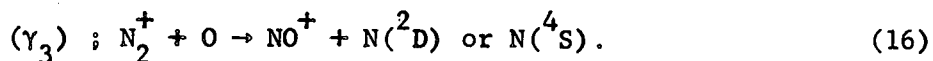
The process which is operative is ionization of  $N_2$  and O followed by dissociative recombination and ion-neutral reactions of  $N_2^+$  and  $O^+$ , [see Nicolet, 1965b],



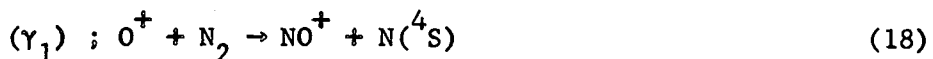
with



and

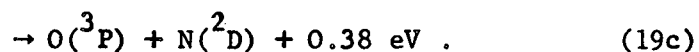
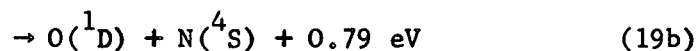
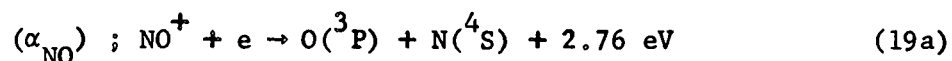


with





and finally



Considering all the possibilities for the production of nitrogen atoms, we have that

$$2 P(N_2) = 2 n(N_2) [J_{N_2} + X I_{N_2}] + 2 n(O) Y I_O \quad (20)$$

where X and Y correspond to the fraction of ionized nitrogen molecules and oxygen atoms leading to excited and normal nitrogen atoms, respectively. With numerical values of  $\gamma$  [Ferguson et al, 1965]

$$X = \frac{n(O) + 10^3 n_e}{n(O) + 10^3 n_e + n(O_2)/2.5} \quad (21)$$

and

$$Y = \frac{n(N_2)}{n(N_2) + 10 n(O_2)} \quad (22)$$

In the  $F_1$  layer where  $n(O) > n(O_2)$ ,  $X \simeq 1$ ; in the E layer, X is about 1/2 between 100 km and 105 km and reaches only 1/5 at 90 km. Y is about 1/2 at 120 km and increases rapidly upward to its limit of 1.

If there is no independent production of nitric oxide, i.e. if reactions such as (1) are negligible and if  $P(NO)$  in (11) or (12) is neglected, the equilibrium value for the concentration of nitric oxide is given by (7c) or

$$n_*(\text{NO}) = \frac{n(\text{N}_2) X I_{\text{N}_2} + n(\text{O}) Y I_{\text{O}}}{b_6 n(\text{N})} = \frac{b_7 n(\text{O}_2)}{b_6} \quad (23)$$

and we have that, also in equilibrium,

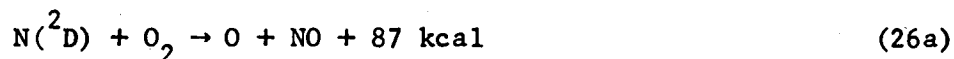
$$n_*(\text{N}) = \frac{n(\text{N}_2) X I_{\text{N}_2} + n(\text{O}) Y I_{\text{O}}}{b_7 n(\text{O}_2)} \quad (24)$$

Above the E layer (Fig. 1) both concentrations depend strongly on the solar activity which leads to concentrations of about  $10^7 \text{ cm}^3$  for average conditions. However, since  $n(\text{NO}) < n(\text{N})$  there is no possibility of an important downward transport of nitric oxide molecules or nitrogen atoms. Above 130 km, the removal of atomic nitrogen occurs through reaction (3) and molecular nitrogen is reformed by reaction (6). A downward transport of nitric oxide requires the following condition in the  $F_1$  layer

$$n(\text{NO}) > n(\text{N}) \quad (25)$$

which is possible only if there is a direct production of nitric oxide of the same order of magnitude as the production of nitrogen atoms.

Of great significance is the production of NO by the reaction



which is more important than the deactivation process



According to Lin and Kaufman [1969] the rate coefficient for the removal of excited atoms  $^2\text{D}$  by (26) is

$$b_{\text{N}}^* = 5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (26b)$$

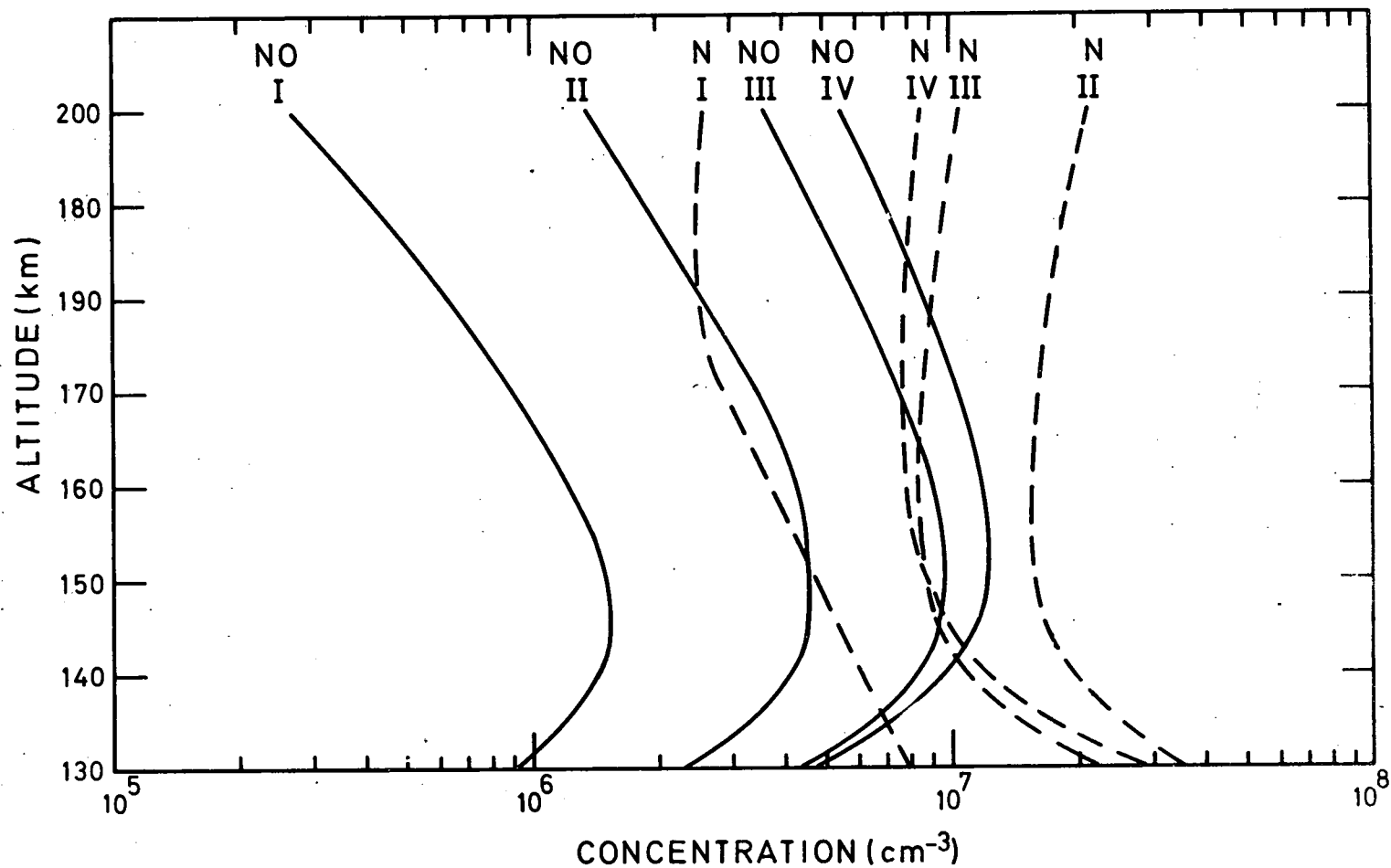
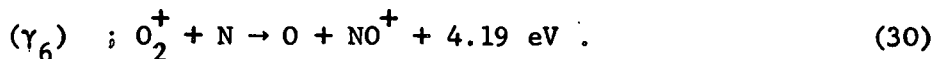
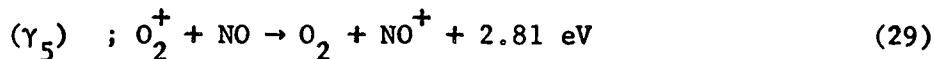
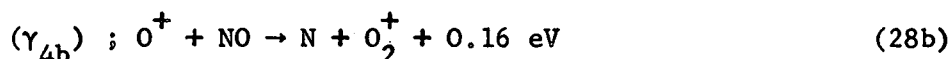
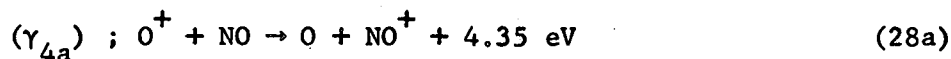


Fig. 1.- Nitric oxide and atomic nitrogen concentrations for photoequilibrium conditions.  
 — Ionization processes correspond to an overhead Sun. I, very quiet Sun and thermopause temperature = 750°K ; II, low average conditions and 1000°K ; III, high average conditions and 1250°K ; IV, high activity and 1500°K.

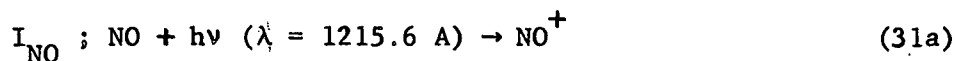
An almost identical value ( $7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ ) has been obtained by Black et al. [1969] who find also that the quenching coefficient by  $\text{N}_2$  is not more than  $6 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ .

On the other hand, the measurements of  $\lambda$  5200 A in the airglow spectrum [Courtès, 1950 ; Dufay, 1951 ; Bates 1952 ; Wallace and McElroy, 1966 ; Weill 1967 ; Hernandez and Turtle, 1969] give a clear indication that the abundance of atomic nitrogen in the excited state  $^2\text{D}$  depends on dissociative recombination processes and associated ionic reactions. Thus, a detailed study of the nitric oxide production based upon observed  $\text{N}(^2\text{D})$  concentrations will be possible when enough observational results on the vertical distribution of excited nitrogen atoms [Wallace and McElroy, 1966] are available.

A detailed study of the nitric oxide abundance based upon a direct source such as (26) requires a modification of equation (10) and (11). In addition to the reactions considered above, it is necessary to include the removal of nitric oxide by other processes such as

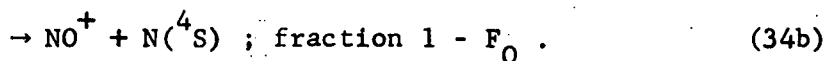
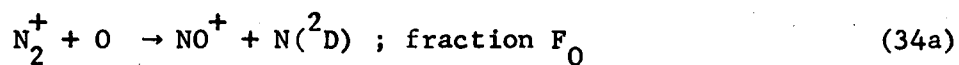
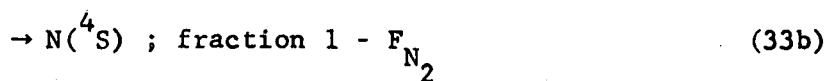
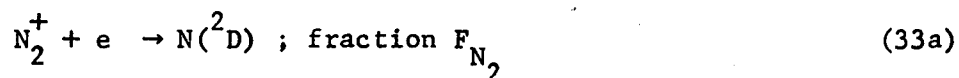
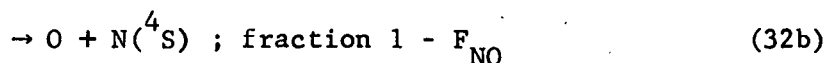
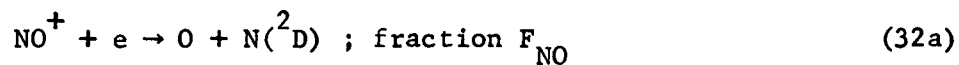


#### Photoionization



with a coefficient  $I_{\text{NO}}$  of the order of  $5 \times 10^{-7} \text{ sec}^{-1}$  must also be considered. Furthermore, the following branching ratios must be taken

into account :



With (28) to (34), we have instead of (10) and (11) that

$$\begin{aligned} \frac{dn(\text{N})}{dt} + n(\text{N}) [b_6 n(\text{NO}) + b_7 n_7 + \gamma_6 n^+(\text{O}_2) F_{\text{NO}}] = \\ n(\text{NO}) \left[ J_{\text{NO}} + \gamma_{4b} n^+(\text{O}) + \left\{ 1 - F_{\text{NO}} \right\} \left\{ I_{\text{NO}} + \gamma_{4a} n^+(\text{O}) + \gamma_5 n^+(\text{O}_2) \right\} \right] \\ + 2 n(\text{N}_2) \left[ J_{\text{N}_2} + X I_{\text{N}_2} \left\{ 1 - F_{\text{N}_2} \right\} \right] + n(\text{O}) Y I_{\text{O}} \left\{ 2 - F_{\text{NO}} \right\} \\ + n^+(\text{N}_2) \gamma_3 n(\text{O}) \left\{ 2 F_{\text{N}_2} - F_{\text{NO}} - F_{\text{O}} \right\} \end{aligned} \quad (35)$$

$$\begin{aligned} \frac{dn(\text{NO})}{dt} + n(\text{NO}) \left[ J_{\text{NO}} + b_6 n(\text{N}) + \gamma_{4b} n^+(\text{O}) + \right. \\ \left. \left\{ 1 - F_{\text{NO}} \right\} \left\{ I_{\text{NO}} + \gamma_{4a} n^+(\text{O}) + \gamma_5 n^+(\text{O}_2) \right\} \right] = \\ n(\text{N}) b_7 n_7 + 2n(\text{N}_2) X I_{\text{N}_2} F_{\text{N}_2} + n(\text{O}) Y I_{\text{O}} F_{\text{NO}} + \\ n^+(\text{N}_2) \gamma_3 n(\text{O}) \left\{ F_{\text{O}} + F_{\text{NO}} + 2 F_{\text{N}_2} \right\} + n^+(\text{O}_2) \gamma_6 n(\text{N}) F_{\text{NO}} . \end{aligned} \quad (36)$$

In order to evaluate the importance of the reaction of excited nitrogen atoms with molecular oxygen on the NO and N concentrations, we assume (see Fig. 2) that  $F_{NO} = 1$ , i.e. that practically all the dissociative recombination of  $NO^+$  leads to  $N(^2D)$ . With  $F_{N_2} = 1/2$  we consider that the dissociative recombination of  $N_2^+$  gives almost equal proportions of  $^2D$  and  $^4S$  nitrogen atoms, and with  $F_O = 0$ , we assume that the reaction of  $O^+$  with  $N_2$  is not important for the production of excited atoms  $N(^2D)$ . Thus, with the working hypothesis  $F_{NO} = 1$ ,  $F_{N_2} = 1/2$  and  $F_O = 0$  adopted in order to simplify (35) and (36), we may write

$$\begin{aligned} \frac{dn(N)}{dt} + n(N) [b_6 n(NO) + b_7 n_7 + \gamma_6 n^+(O_2)] = \\ n(NO) [J_{NO} + \gamma_{4b} n^+(O)] + n(N_2) [2 J_{N_2} + Y I_{N_2}] + n(O) Y I_O \end{aligned} \quad (37)$$

$$\begin{aligned} \frac{dn(NO)}{dt} + n(NO) [J_{NO} + b_6 n(N) + \gamma_{4b} n^+(O)] = \\ n(N) b_7 n_7 + n(N_2) X I_{N_2} + n(O) Y I_O + n^+(O_2) \gamma_6 n(N) \end{aligned} \quad (38)$$

or

$$\begin{aligned} \frac{dn(NO)}{dt} + \frac{dn(N)}{dt} + 2b_6 n(N) n(NO) = \\ 2 n(N_2) [J_{N_2} + X I_{N_2}] + 2 n(O) Y I_O \end{aligned} \quad (39)$$

$$\begin{aligned} \frac{dn(NO)}{dt} - \frac{dn(N)}{dt} + 2n(NO) [J_{NO} + \gamma_{4b} n^+(O)] + 2n(N_2) J_{N_2} = \\ 2 n(N) [b_7 n_7 + \gamma_6 n^+(O_2)]. \end{aligned} \quad (40)$$

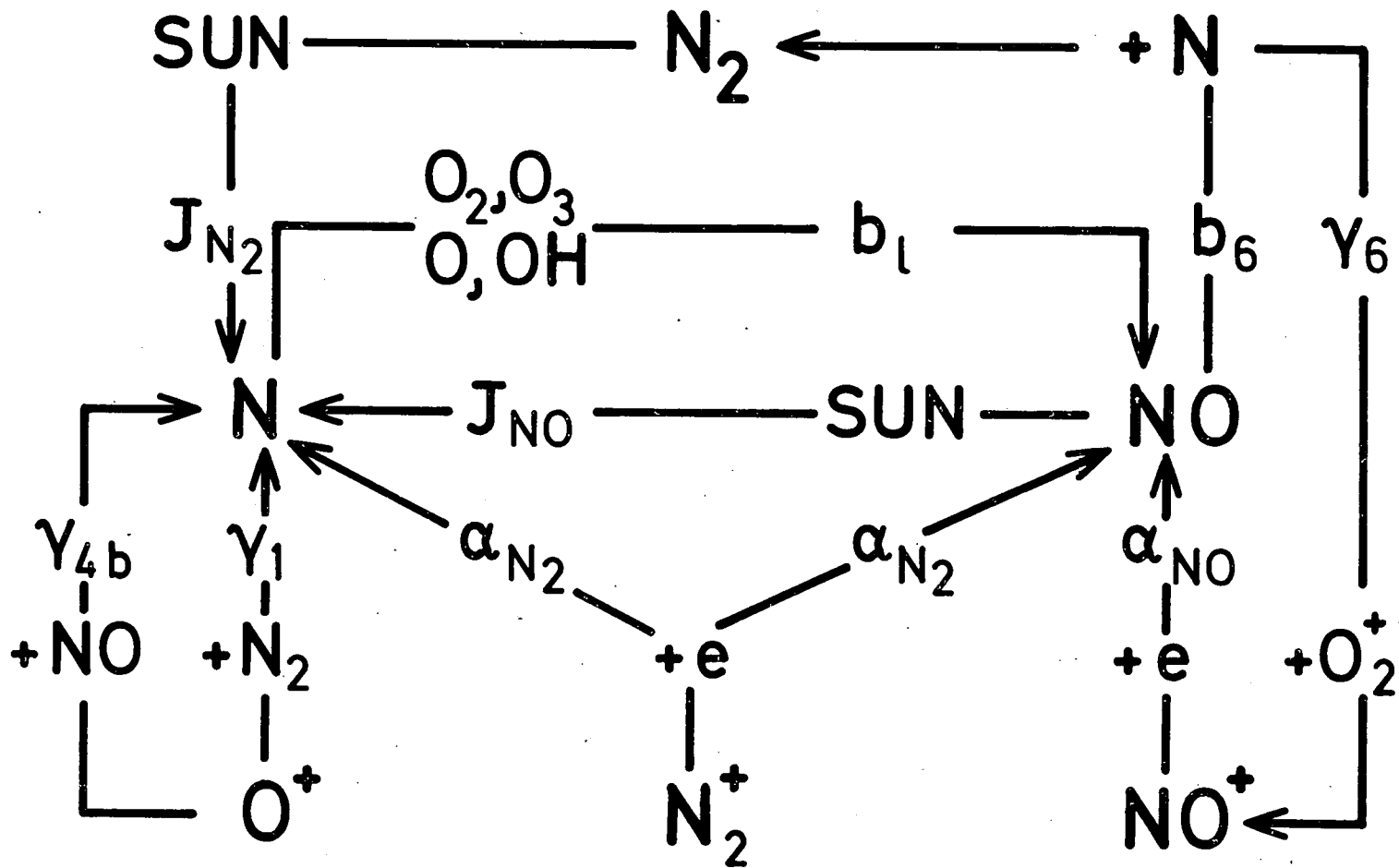


Fig. 2.- Reactions of formation and removal of nitric oxide and atomic nitrogen. Excited atoms N(<sup>2</sup>D) are involved in the NO production through the dissociative recombination of N<sub>2</sub><sup>+</sup> and NO<sup>+</sup>.

We have that in equilibrium

$$n(N) [b_7 n_7 + \gamma_6 n^+(O_2)] = n(NO) [J_{NO} + \gamma_{4b} n^+(O)] + n(N_2) J_{N_2} \quad (41)$$

$$b_6 n(NO) n(N) = n(N_2) [J_{N_2} + X I_{N_2}] + n(O) Y I_O \quad (42)$$

In the E layer the photodissociation of  $N_2$  and the reaction between N and  $O_2^+$  influence the ratio  $n(NO)/n(N)$ ; in the F region, their effect is negligible. Thus, above the E layer, the photoequilibrium conditions correspond to

$$\frac{n(NO)}{n(N)} = \frac{b_7 n(O_2)}{J_{NO} + b_{4b} n^+(O)} \quad (43)$$

and

$$n^2(NO) = \frac{b_7 n(O_2)}{b_6} \frac{n(N_2) X I_{N_2} + n(O) Y I_O}{J_{NO} + b_{4b} n^+(O)} \quad (44)$$

Since  $J_{NO} = 5 \times 10^{-6} \text{ sec}^{-1}$  and  $b_7 n(O_2) > J_{NO}$  it is clear that there is a possibility that  $n(NO) > n(N)$  in the thermosphere above the E layer. Again since  $b_7 n(O_2)/b_6 = n_*(NO)$ , any increase above the chemical value is related to the ionic production leading to  $N(^2D)$  atoms.

With the positive ion production rates which have been used to derive the N and NO concentrations shown in Figure 1, it is possible to derive the N and NO concentrations corresponding to (43) and (44). Figure 3, which is to be compared with Figure 1, shows how important is the production of nitric oxide molecules other than from normal nitrogen atoms. Other solutions can be obtained if the branching ratio of the production of  $^2D$  and  $^4S$  nitrogen atoms is varied. The NO and N concentrations are sensitive to the variation of the branching ratio, but they depend also on the variations of the solar flux and of the



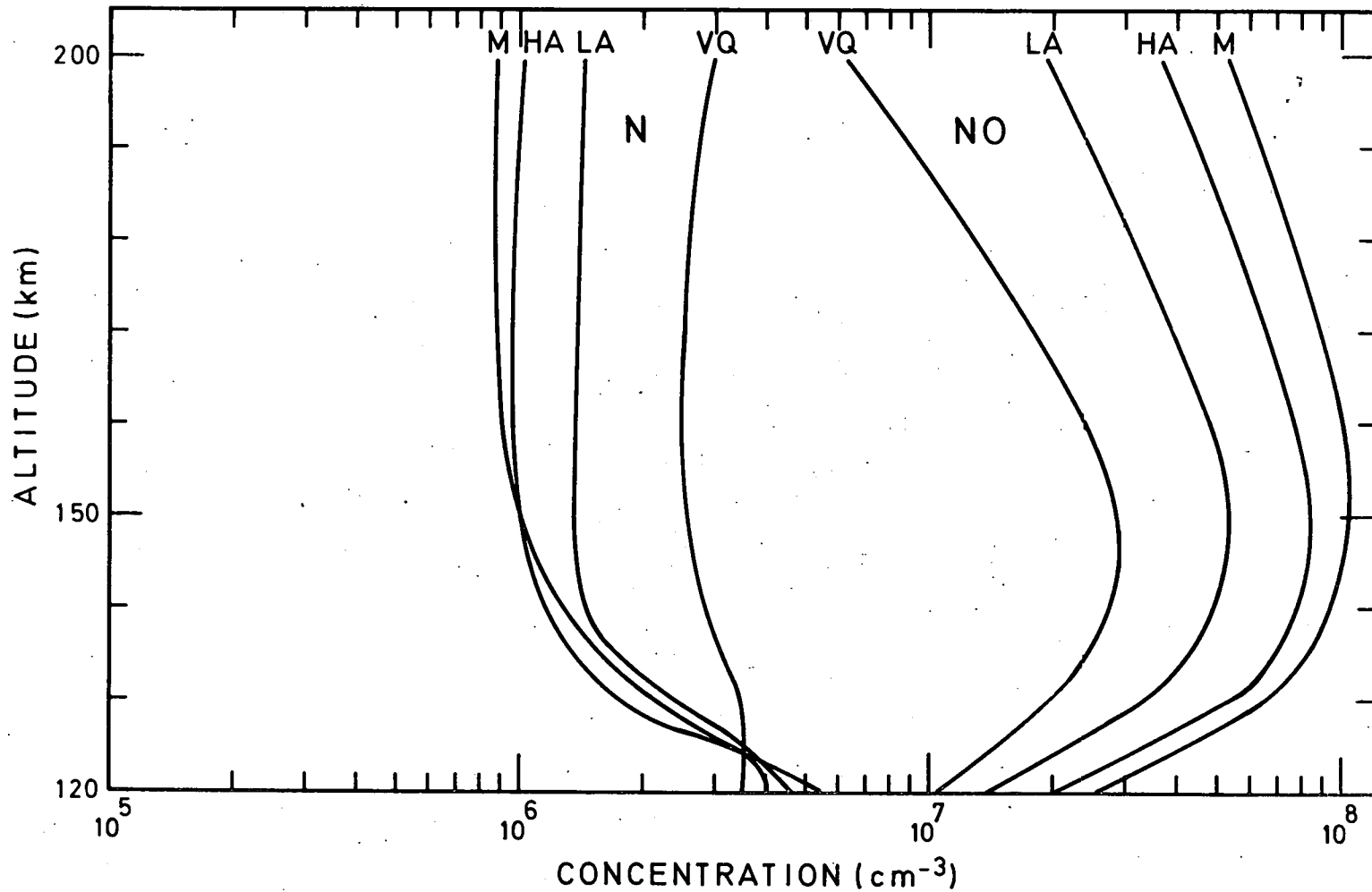


Fig. 3.- Nitric oxide and atomic nitrogen concentrations for photoequilibrium conditions.  
 Ionization processes as in Fig. 1. Effect of the  $N(^2D) + O_2$  reaction on the formation of nitric oxide.

thermospheric temperature.

In order to interpret the results shown in Figure 3 it is necessary to consider the modifications which are required by a departure from photochemical equilibrium conditions. Not surprisingly, with concentrations of nitric oxide greater than the chemical equilibrium values, atomic nitrogen is practically in photochemical equilibrium in the sunlit F layer. After sunset, a rapid decrease occurs since its production is negligible compared with its removal. But nitric oxide cannot reach its photochemical equilibrium value and dynamic processes are therefore involved. With a molecular diffusion coefficient of the order of  $(3 \pm 1) \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$  corresponding to the NO concentration peak (150-160 km) for an overhead Sun, the diffusion time  $\tau_D = H^2/D$  is about  $(3 \pm 1) \times 10^4$  sec, i.e a value which leads to a downward transport of nitric oxide molecules. This crude estimate of the diffusion time demonstrates that the nitric oxide concentration in the lower thermosphere (in the E layer) depends on its downward transport by molecular diffusion in the F layer and is greater than the photochemical values. In the lower thermosphere the downward current of NO molecules depends on the value of the eddy diffusion coefficient. In any case, this current is to replace the nitric oxide molecules destroyed through the photodissociation in the mesosphere. In the stratosphere the final sink of NO (and NO<sub>2</sub>) is the formation of HNO<sub>2</sub> and HNO<sub>3</sub> [Nicolet, 1965a, 1969] by reactions with HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> since no photodissociation process occur below the stratopause. A small eddy diffusion coefficient is required.

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