the particle density and a total optical thickness $T = 2$. With the IBM 360–91 computer it takes about 20 min to simulate the life histories of 10^7 photons.

4. CONCLUSIONS

The comparison of the model calculations with the observed profile shows that the model can be used for the interpretation of observations. The consideration of different phase angles, high scattering numbers and different density distributions are the main points of these calculations. This model is used in a current work for the interpretation of the photographic and photoelectric measurements, which were performed at the rocket-experiment in Kiruna 1969.

Ruhr-Universität Bochum   H. M. Kappler
Bereich Extraterrestrische Physik
Buscheystrasse
463 Bochum
W. Germany

REFERENCES

Föppl, H., Haerendel, G., Haser, L., Loidl, J., Lütjens, P., Lüst, R., Melzner, F., Meyer, B., Neuss, H. and Rieger, E. (1967). *Planet. Space Sci.* **15**, 357–372.
Giese, R.-H. and Smilga, W. (1967). *Ann. Met.* **3**, 37.
Hammersley, J. M. and Handscomb, D. C. (1964). *Monte Carlo Meth. Methuen's Monogr.*
Haser, L. (1967). *Aurora and Airglow, Proc. Nato advanced Study Inst.* S.391–403.
Jansson, B. (1966). *Random Number Generators.* Stockholm.
Lloyd, K. H. (1965). *Aust. J. Phys.* **18**, 349–362.

THE ORIGIN OF NITRIC OXIDE IN THE TERRESTRIAL ATMOSPHERE

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).
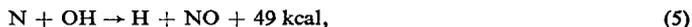
In order to increase the source or nitric oxide in the lower thermosphere Nicolet (1965b) suggested the possibility of an indirect way of production by the following reaction

$$O_2^+ + N_2 \rightarrow NO^+ + NO + 16 \, kcal \tag{1}$$

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 $10^{-15} \, cm^3 \, sec^{-1}$ at several hundred degrees. Hunten and McElroy (1968) after rejecting the proceding reaction proposed as an alternative reaction

$$N + O_2 \, (^1\Delta_g) \rightarrow O + NO + 54 \, kcal. \tag{2}$$
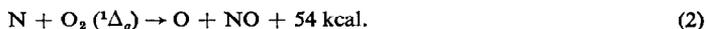
This cannot be accepted as the source since the free nitrogen atoms are involved in normal aeronomic processes such as

$$N + O_2 \rightarrow O + NO + 32 \, kcal \tag{3}$$

$$N + O_3 \rightarrow O_2 + NO + 126 \, kcal \tag{4}$$

$$N + OH \rightarrow H + NO + 49 \, kcal, \tag{5}$$

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 $2 \times 10^{-15} \, cm^3 \, sec^{-1}$ at $200°K$, shows clearly that the analysis by

Hunten 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:

$$N + NO \rightarrow O + N_2 + 75 \text{ kcal} \tag{6a}$$

with a rate coefficient

$$b_6 = (1{\cdot}5 \pm 0{\cdot}5) \times 10^{-12}\, T^{1/2}\, \text{cm}^3\, \text{sec}^{-1} \tag{6b}$$

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*

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

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

$$b_7 n(O_2) = 5 \times 10^{-13}\, T^{1/2}\, e^{-3500/T}\, n(O_2)\, \text{sec}^{-1} \tag{7b}$$

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

$$n_*(NO) = 3 \times 10^{-1}\, e^{-3500/T}\, n(O_2)\, \text{cm}^{-3} \tag{7c}$$

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

$$NO + h\nu\ (\lambda < 1905\ \text{A}) \rightarrow N + O \tag{8a}$$

corresponds to a predissociation observed in the γ, β, δ and ε 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

$$J_{NO} = 5 \times 10^{-6}\ \text{sec}^{-1}. \tag{8b}$$

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

$$\frac{n(NO)}{n(N)} = \frac{b_7 n(O_2)}{J_{NO} + b_6 n(N)}. \tag{9a}$$

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

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

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

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

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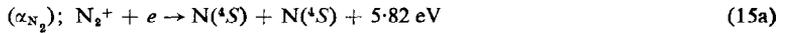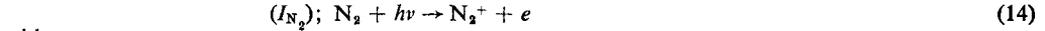
$$\frac{dn(N)}{dt} + \frac{dn(NO)}{dt} + 2b_6 n(NO)\, n(N) = 2P(N_2) + P(NO). \tag{12}$$

Atomic nitrogen is produced by a predissociation process (Herzberg and Herzberg, 1948; Bates, 1954) with a rate coefficient for zero optical depth
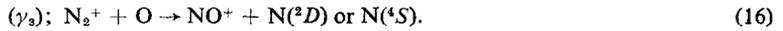
$$J_{N_2} = 5 \times 10^{-14} \ \text{sec}^{-1} \tag{13}$$

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),
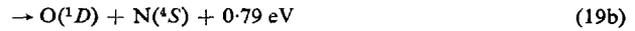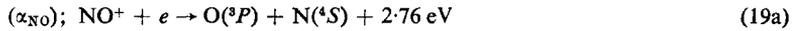
$$(I_{N_2}); \ N_2 + h\nu \rightarrow N_2^+ + e \tag{14}$$

with

$$(\alpha_{N_2}); \ N_2^+ + e \rightarrow N(^4S) + N(^4S) + 5 \cdot 82 \ \text{eV} \tag{15a}$$

$$\rightarrow N(^4S) + N(^2D) + 3 \cdot 44 \ \text{eV} \tag{15b}$$

$$\rightarrow N(^4S) + N(^2P) + 2 \cdot 24 \ \text{eV} \tag{15c}$$

$$\rightarrow N(^2D) + N(^2D) + 1 \cdot 06 \ \text{eV} \tag{15d}$$

and

$$(\gamma_3); \ N_2^+ + O \rightarrow NO^+ + N(^2D) \ \text{or} \ N(^4S). \tag{16}$$

$$(I_0); \ O + h\nu \rightarrow O^+ + e \tag{17}$$

with

$$(\gamma_1); \ O^+ + N_2 \rightarrow NO^+ + N(^4S) \tag{18}$$

and finally

$$(\alpha_{NO}); \ NO^+ + e \rightarrow O(^3P) + N(^4S) + 2 \cdot 76 \ \text{eV} \tag{19a}$$

$$\rightarrow O(^1D) + N(^4S) + 0 \cdot 79 \ \text{eV} \tag{19b}$$

$$\rightarrow O(^3P) + N(^2D) + 0 \cdot 38 \ \text{eV}. \tag{19c}$$

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

$$2P(N_2) = 2n(N_2) [J_{N_2} + XI_{N_2}] + 2n(O) \ YI_0 \tag{20}$$

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 γ (Ferguson *et al.*, 1965)

$$X = \frac{n(O) + 10^3 n_e}{n(O) + 10^3 n_e + n(O_2)/2 \cdot 5} \tag{21}$$

and

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

In the $F1$-layer where $n(O) > n(O_2)$, $X \simeq 1$; in the E-layer, X is about $\frac{1}{2}$ between 100 km and 105 km and reaches only $\frac{1}{5}$ at 90 km. Y is about $\frac{1}{2}$ 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

$$n_*(NO) = \frac{n(N_2)XI_{N_2} + n(O) \ YI_0}{b_6 n(N)} = \frac{b_7 n(O_2)}{b_6}. \tag{23}$$

and we have that, also in equilibrium,

$$n_*(N) = \frac{n(N_2)XI_{N_2} + n(O) \ YI_0}{b_7 n(O_2)}. \tag{24}$$

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 $n(NO) < n(N)$ 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 $F1$-layer
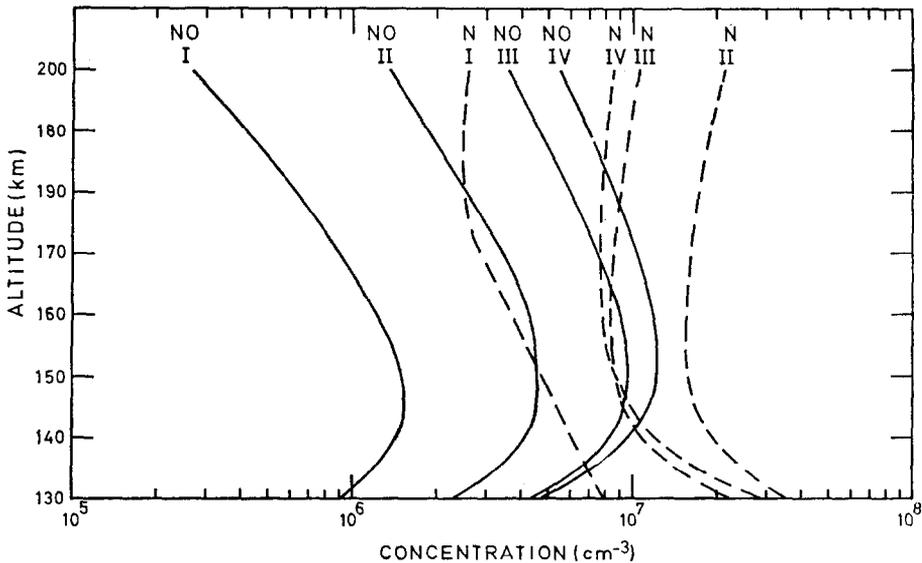
$$n(NO) > n(N) \tag{25}$$

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 $1500°K$.

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

$$N(^2D) + O_2 \rightarrow O + NO + 87 \text{ kcal} \tag{26a}$$
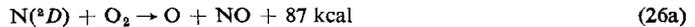
which is more important that the deactivation process

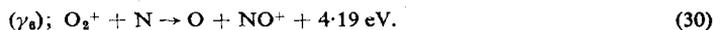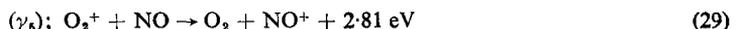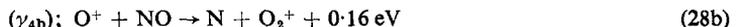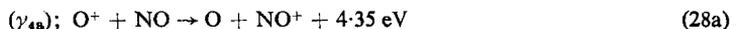$$N(^2D) + O_2 \rightarrow O_2 + N(^4S). \tag{27}$$

According to Lin and Kaufman (1969) the rate coefficient for the removal of excited atoms ^2D by (26) is

$$b_N{}^* = 5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}. \tag{26b}$$

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 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 ^2D depends on dissociative recombination pro-
cesses and associated ionic reactions. Thus, a detailed study of the nitric oxide production based upon
observed $N(^2D)$ concentrations will be possible when enough observational results on the vertical distribution
of excited nitrogen atoms (cf., Wallace and McElroy, 1966) are available.

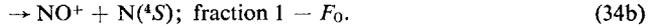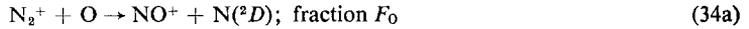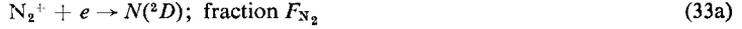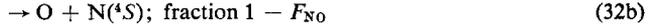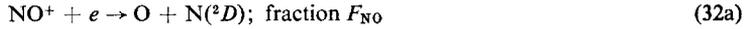A detailed study of the nitric oxide abundance based upon a direct source such as (26) requires a modi-
fication of Equations (10) and (11). In addition to the reactions considered above, it is necessary to include
the removal of nitric oxide by other processes such as

$$(\gamma_{4a}); \quad O^+ + NO \rightarrow O + NO^+ + 4·35 \text{ eV} \tag{28a}$$

$$(\gamma_{4b}); \quad O^+ + NO \rightarrow N + O_2{}^+ + 0·16 \text{ eV} \tag{28b}$$

$$(\gamma_5); \quad O_2{}^+ + NO \rightarrow O_2 + NO^+ + 2·81 \text{ eV} \tag{29}$$

$$(\gamma_6); \quad O_2{}^+ + N \rightarrow O + NO^+ + 4·19 \text{ eV}. \tag{30}$$

Photoionization

$$I_{NO}; \quad NO + h\nu \ (\lambda = 1215·6 \text{ A}) \rightarrow NO^+ \tag{31a}$$

with a coefficient I_{NO} of the order of 5×10^{-7} sec^{-1} must also be considered. Furthermore, the following branching ratios must be taken into account:

$$NO^+ + e \to O + N(^2D); \text{ fraction } F_{NO} \tag{32a}$$

$$\to O + N(^4S); \text{ fraction } 1 - F_{NO} \tag{32b}$$

$$N_2^+ + e \to N(^2D); \text{ fraction } F_{N_2} \tag{33a}$$

$$\to N(^4S); \text{ fraction } 1 - F_{N_2} \tag{33b}$$

$$N_2^+ + O \to NO^+ + N(^2D); \text{ fraction } F_O \tag{34a}$$

$$\to NO^+ + N(^4S); \text{ fraction } 1 - F_O. \tag{34b}$$

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

$$\frac{dn(N)}{dt} + n(N)\,[b_6 n(NO) + b_7 n_7 + \gamma_6 n^+(O_2)F_{NO}]$$

$$= n(NO)\,[J_{NO} + \gamma_{4b} n^+(O) + \{1 - F_{NO}\}\{I_{NO} + \gamma_{4a} n^+(O) + \gamma_5 n^+(O_2)\}]$$

$$+ 2n(N_2)[J_{N_2} + XI_{N_2}\{1 - F_{N_2}\}] + n(O)\,YI_0\,\{2 - F_{NO}\}$$

$$+ n^+(N_2)\gamma_3 n(O)\,\{2F_{N_2} - F_{NO} - F_O\} \tag{35}$$

$$\frac{dn(NO)}{dt} + n(NO)[J_{NO} + b_6 n(N) + \gamma_{4b} n^+(O) + \{1 - F_{NO}\}\{I_{NO} + \gamma_{4a} n^+(O) + \gamma_5 n^+(O_2)\}]$$

$$= n(N)b_7 n_7 + 2n(N_2)XI_{N_2}F_{N_2} + n(O)YI_0 F_{NO} + n^+(N_2)\gamma_3 n(O)$$

$$\times \{F_O + F_{NO} + 2F_{N_2}\} + n^+(O_2)\gamma_6 n(N)F_{NO} . \tag{36}$$
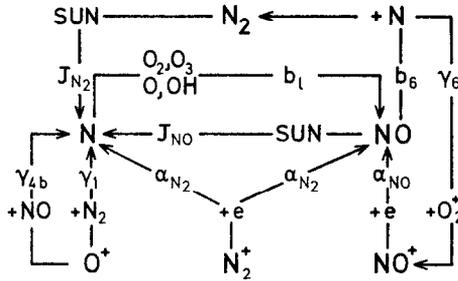

FIG. 2. REACTIONS OF FORMATION AND REMOVAL OF NITRIC OXIDE AND ATOMIC NITROGEN
Excited atoms $N(^2D)$ are involved in the NO production through the dissociative recombination
of N_2^+ and NO^+.

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 $F_{N_2} = \frac{1}{2}$ 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 $F_{NO} = 1$, $F_{N_2} = \frac{1}{2}$ and $F_O = 0$ adopted in order to simplify (35) and (36), we may write

$$\frac{dn(N)}{dt} + n(N)[b_6 n(NO) + b_7 n_7 + \gamma_6 n^+(O_2)]$$

$$= n(NO)[J_{NO} + \gamma_{4b} n^+(O)] + n(N_2)[2J_{N_2} + YI_{N_2}] + n(O)YI_0 \tag{37}$$

$$\frac{dn(NO)}{dt} + n(NO)[J_{NO} + b_6 n(N) + \gamma_{4b} n^+(O)]$$

$$= n(N)b_7 n_7 + n(N_2)XI_{N_2} + n(O)YI_0 + n^+(O_2)\gamma_6 n(N) \tag{38}$$

or

$$\frac{dn(NO)}{dt} + \frac{dn(N)}{dt} + 2b_6 n(N)\, n(NO) = 2n(N_2)[J_{N_2} + XI_{N_2}] + 2n(O)\, YI_0 \qquad (39)$$

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

We have that in equilibrium

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

$$b_6 n(NO)n(N) = n(N_2)[J_{N_2} + XI_{N_2}] + n(O)\, YI_0. \qquad (42)$$

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

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

and

$$n^2(NO) = \frac{b_7 n(O_2)}{b_6}\, \frac{n(N_2)XI_{N_2} + n(O)\, YI_0}{J_{NO} + b_{4b}n^+(O)}. \qquad (44)$$

Since $J_{NO} = 5 \times 10^{-6}$ 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 Fig. 1, it is possible to derive the N and NO concentrations corresponding to (43) and (44). Figure 3, which is to be compared with Fig. 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
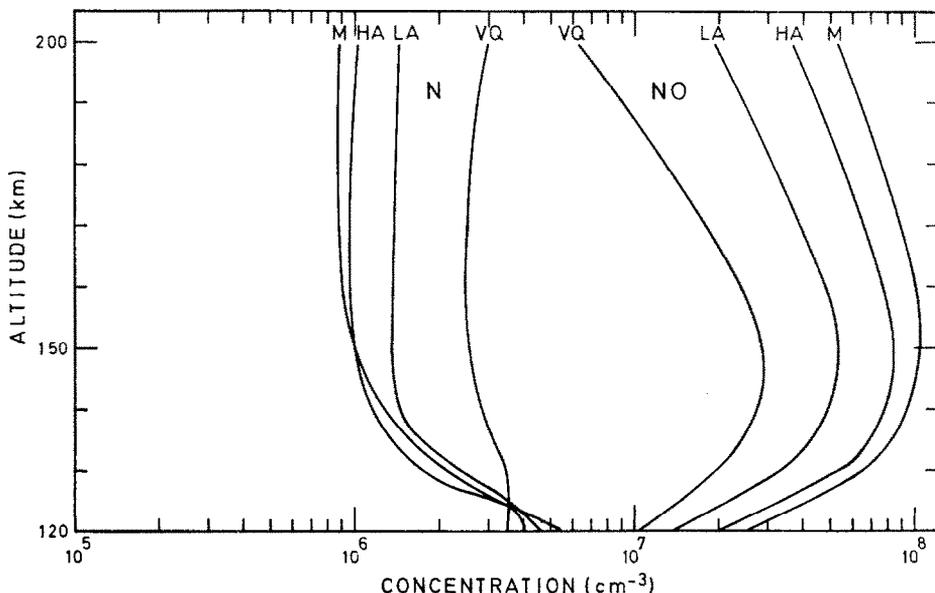

FIG. 3. NITRIC OXIDE AND ATOMIC NITROGEN CONCENTRATIONS FOR PHOTOEQUILIBRIUM CONDITIONS.
Effect of the $N(^2D) + O_2$ reaction on the formation of nitric oxide. Ionization processes correspond to an overhead Sun. VQ, very quiet Sun and thermopause temperature $= 750°K$; LA, low average conditions and $1000°K$; HA, high average conditions and $1250°K$; M, high activity and $1500°K$.

^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 thermospheric temperature.

In order to interpret the results shown in Fig. 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 $(3 \pm 1) \times 10^3$ cm^2 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 value. 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$_2$) is the formation of HNO$_2$ and HNO$_3$ (Nicolet 1965a, 1969) by reactions with HO$_2$ and H$_2$O$_2$ since no photodissociation process occur below the stratopause. A small eddy diffusion coefficient is required.

Institut d'Aéronomie Spatiale
Avenue Circulaire 3
1180 *Bruxelles*
Belgium

M. NICOLET

REFERENCES

BARTH, C. A. (1961). Nitrogen and oxygen atomic reactions in the chemosphere. In *Chemical Reactions in the Lower and Upper Atmosphere*, p. 303. Interscience, New York.

BARTH, C. A. (1964). Rocket measurement of the nitric oxide airglow. *J. geophys. Res.* **69**, 3301.

BARTH, C. A. (1966). Nitric oxide in the upper atmosphere. *Annls Géophys.* **22**, 198.

BATES, D. R. (1952). Some reactions occurring in the Earth's upper atmosphere. *Annls Géophys.* **8**, 194.

BATES, D. R. (1954). The physics of the upper atmosphere. In *The Earth as a Planet*, Chap. 2. Universities Chicago Press, Chicago.

BLACK, G., SLANGER, T. G., ST. JOHN, G. A. and YOUNG, R. A. (1969). Deactivation of N(^2D). *J. Chem. Phys.* **51**, 116.

CALLEAR, A. B. and SMITH, I. W. M. (1964). Determination of the rate constants for predissociation collisional quenching and spontaneous radiation of NO C^2 Π ($v = 0$). *Disc. Faraday Soc.* **37**, 96.

CLARK, I. D. and WAYNE, R. P. (1969). The reaction of O$_2$($^1\Delta_g$) with atomic nitrogen and with atomic oxygen. *Chem. Phys. Lett.* **3**, 405.

COURTÈS, G. (1950). La raie ^4S–^2D de l'azote observée au crépuscule. *C. r. Acad. Sci.* **231**, 62.

DUFAY, M. (1951). La raie interdite ^4S–^2D de l'atome neutre d'azote dans les spectres du ciel nocturne et du crépuscule. *C. r. Acad. Sci.* **233**, 419.

FERGUSON, E. E. (1967). Ionospheric ion–molecule reaction rates. *Rev. Geophys.* **5**, 305.

FERGUSON, E. E., FEHSENFELD, F. C., GOLDAN, P. D., SCHMELTEKOPF A. L. and SCHIFF H. I. (1965). Laboratory measurement of the rate of the reaction N$_2^+$ + O → NO$^+$ + N at thermal energy. *Planet. Space Sci.* **13**, 823.

FINDLAY, F. D., FORTIN, C. J. and SNELLING, D. R. (1969). Deactivation of O$_2$($^1\Delta_g$). *Chem. Phys. Lett.* **3**, 20.

HEICKLEN, J. and COHEN, N. (1968). The role of nitric oxide in photochemistry. *Adv. Photochem.* **5**, 303.

HERNANDEZ, G. and TURTLE, J. P. (1969). The NI($^4S^0_{3/2} - {}^2D^0_{5/2,3/2}$) transitions in the upper atmosphere at night. *Planet. Space Sci.* **17**, 675.

HERZBERG, G. and HERZBERG, L. (1948). Production of nitrogen atoms in the upper atmosphere. *Nature, Lond.* **161**, 283.

HUNTEN, D. M. and McELROY, M. B. (1968). Metastable O$_2$($^1\Delta_g$) as a major source of ions in the D-region. *J. geophys. Res.* **73**, 241.

LIN, C. L. and KAUFMAN, F. (1970). Deactivation and reaction of N(^2D). *J. chem. Phys.* To be published.

NICOLET, M. (1945). L'interprétation physique de l'ionosphère. *Mém. Inst. r. mét. Belg.* **19**, 106.

NICOLET, M. (1955). The aeronomic problem of nitrogen oxides. *J. atmos. terr. Phys.* **7**, 255.

NICOLET, M. (1965a). Nitrogen oxides in the chemosphere. *J. geophys. Res.* **70**, 679.

NICOLET, M. (1965b). Ionospheric processes and nitric oxide. *J. geophys. Res.* **70**, 691.

NICOLET, M. (1970). Ozone and hydrogen reactions. *Annls Géophys.* **26** (paper presented at the IAGA Assembly, Madrid September, 1969).

NICOLET, M. and AIKIN A. C. (1960). The formation of the D-region of the ionosphere. *J. geophys. Res.* **65**, 1469.

PEARCE, J. B. (1969) Rocket measurement of nitric oxide between 60 and 96 km. *J. geophys. Res.* **74**, 853.

PHILIPS, L. F. and SCHIFF, H. I. (1962). Reactions in the atomic nitrogen–ozone systems. *J. chem. Phys.* **36,** 1509.

PONTANO, B. A. and HALE, L. E. (1970). Measurement of an ionizable constituent of the low ionosphere using a Lyman-α source and blunt probe. *Space Research X.* North-Holland, Amsterdam.

SCHIFF, H. I. (1969). Neutral reactions involving oxygen and nitrogen. *Can. J. Chem.* **47,** 1903.

VLASTARAS, A. S. and WINKLER, C. A. (1967). Reaction of active nitrogen with oxygen. *Can. J. Chem.* **45,** 2837.

WALLACE, L. and McELROY, M. B. (1966). The visual dayglow. *Planet. Space Sci.* **14,** 677.

WEILL, G. (1967). La recombinaison nocturne de la région ionosphérique F-observée optiquement. *C. r. Acad. Sci.* **264B,** 1685.

WILSON, W. E. (1967). Rate constant for the reaction $H + O_2 \rightarrow NO + O$. *J. chem. Phys.* **46,** 2017.