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Nitrogen Oxides in the Chemosphere

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Abstract. A study is made of the various reactions in which nitrogen oxides are involved in the chemosphere. The hydrogen compounds do not play an important role, and it is found that the essential aeronomic reactions depend on ozone and atomic oxygen. Thus, the ratio of nitrogen dioxide to nitric oxide can be determined. The absolute values of the NO_2 and NO concentrations depend on the dissociation of molecular nitrogen in the chemosphere. The chemical conditions cannot be applied in the mesosphere, since the lifetime of NO is relatively long, and a downward transport is involved. Very special assumptions about chemical reactions would be necessary to reconcile the photochemical picture and the observational results. The introduction of ionic reactions, considered in an accompanying paper, will lead to a correct interpretation.

Introduction. The subject of nitrogen oxides was introduced [*Nicolet,* 1945] in aeronomic studies of nitric oxide as an important ionic constituent of the ionospheric *D* region. The photochemistry of nitrogen was first studied by *Bates* [1952] and has been further studied by *Bates* [1954] and *Nicolet* [1954]. This problem, which is much more complicated than that of the photochemistry of oxygen, was developed by *Nicolet* [1955] in relation with the airglow. Calculations are difficult, because the chemical aeronomy of nitrogen in an oxygen atmosphere leads to a complex problem, as *Nicolet* [1960] and *Barth* [1961] have recently pointed out. The presence of important concentrations of nitric oxide ions requires a special analysis of ionic reactions related to the presence or absence of the neutral molecule. Our experimental knowledge about rate coefficients is not yet complete, but it has increased rapidly in recent years, and a systematic account can be found in several review papers: three-body reactions by *Barth* [1964], reactions involving nitrogen and oxygen by *Schiff* [1964], and aeronomic reactions involving hydrogen by *Kaufman* [1964].

Attention here will be confined to the photochemistry of nitrogen. Another paper will cover the subject of related ionic reactions which modify the photochemical picture and add greatly to the significance of the occurrence of atomic nitrogen and its oxides in the ionosphere.

Nitrogen dioxide and nitric oxide ratios below 100 kilometers. If nitrogen dissociation is operative at sufficiently low altitudes, the formation of nitric oxide may be due to a three-body process

$$N + O + M \rightarrow NO + M + 150\ \text{kcal} \tag{1}$$

for which the rate coefficient b_{1a} is not yet known with sufficient precision [*Mavroyannis and Winkler,* 1961*a*; *Krestchner and Petersen,* 1963; *Barth,* 1964]. Calculations will be made with the following recombination rate

$$b_{1a} = (1 \pm 0.5) \times 10^{-32} n(M)\ \text{cm}^3\ \text{sec}^{-1} \tag{2}$$

Three-body recombination of nitrogen and oxygen atoms leads to the emission of various electronic bands of nitric oxide [*Barth et al.,* 1959].

A pre-association process such as [*Young and Sharpless,* 1963; *Callear and Smith,* 1964]

$$N(^4S) + O(^3P) \rightarrow NO(^4\Pi) \rightarrow NO(C^2\Pi) \tag{3}$$

followed by

$$NO(C^2\Pi) \rightarrow NO(X^2\Pi) + \gamma\ \text{bands} \qquad A_{21} = 1.5 \times 10^7\ \text{sec}^{-1} \tag{4a}$$

and

$$NO(C^2\Pi) \rightarrow N(^4S) + O(^3P) \qquad a_{21} = 3.5 \times 10^8\ \text{sec}^{-1} \tag{4b}$$

results in nitric oxide formation with a rate coefficient b_{1b},

$$b_{1b} = 1 \times 10^{-17}\ \text{cm}^3\ \text{sec}^{-1} \tag{5}$$

which is more effective than (2) where $n(M)$ is less than 10^{15} cm^{-3}.

On the basis of *Young and Sharpless'* [1963] investigation of the chemiluminescent production of the β, γ, and δ bands, the following absolute rates of the emission processes are obtained:

β bands: $2.4 \times 10^{-34}\, n(\mathrm{M})\, n(\mathrm{O})\, n(\mathrm{N})$ cm^{-3} sec^{-1}

γ bands: $8.2 \times 10^{-18}\, n(\mathrm{N})\, n(\mathrm{O}) + 2.4 \times 10^{-35}\, n(\mathrm{M})\, n(\mathrm{O})\, n(\mathrm{N})$ cm^{-3} sec^{-1} measured at 4 mm Hg.

Before considering other nitric oxide formation processes, it is necessary to simplify the study of nitric oxide by analyzing its reactions with atomic oxygen and ozone, which are the principal active constituents in the chemosphere. First, there is the three-body process

$$\mathrm{O} + \mathrm{NO} + \mathrm{M} \rightarrow \mathrm{NO_2} + \mathrm{M} + 72\ \mathrm{kcal} \qquad (6)$$

The reaction has a relatively high rate coefficient [*Kaufman,* 1958; *Ogryzlo and Schiff,* 1959; *Clyne and Thrush,* 1962c; *Schiff,* 1964; *Reeves et al.,* 1964] with a negative activation energy of about 1.8 ± 0.4 kcal according to *Clyne and Thrush* [1962c] or 1.93 ± 0.1 kcal according to *Klein and Herron* [1964]. The following rate coefficient for (6) is adopted:

$$b_{2a} = 3 \times 10^{-33} e^{1000/T} n(\mathrm{M}) \quad \mathrm{cm^3\, sec^{-1}} \qquad (7)$$

This three-body process leading to the formation of nitrogen dioxide must be compared with the radiative process [*Bates,* 1954; *Nicolet,* 1960]

$$\mathrm{O} + \mathrm{NO} \rightarrow \mathrm{NO_2} + h\nu(\lambda > 3975\ \mathrm{A}) \qquad (8)$$

which should be a three-body mechanism according to various laboratory measurements. The measured rate coefficient (3875 A–1.4 μ) is [*Fontijn et al.,* 1964]

$$b_{2b} = 6.4 \times 10^{-17} \quad \mathrm{cm^3\, sec^{-1}} (\pm 30\%) \qquad (9)$$

For $\lambda < 7250$ A, we consider the following value:

$$b_{2b} = 3.2 \times 10^{-17} \quad \mathrm{cm^3\, sec^{-1}} \qquad (10)$$

Since the probability of emission is not less than 4×10^6 sec^{-1}, we adopt the rate coefficient given by (9) at all altitudes [*Levitt,* 1962; *Schiff,* 1964; *Doherty and Jonathan,* 1964; *Reeves et al.,* 1964].

Two bimolecular processes must be considered as important aeronomic reactions. One is a reaction with oxygen atoms

$$\mathrm{O} + \mathrm{NO_2} \rightarrow \mathrm{NO} + \mathrm{O_2} + 46\ \mathrm{kcal} \qquad (11)$$

This is known to be rapid [*Ford and Endow,* 1957; *Phillips and Schiff,* 1962a; *Schiff,* 1964; *Klein and Herron,* 1964]. The $\mathrm{O_2}$ molecules formed in (11) are vibrationally excited [*Basco and Norrish,* 1960; *Phillips and Schiff,* 1962c] to $v'' = 8$ (33.7 kcal) and perhaps electronically excited to $^1\Sigma_g(v' \leqq 2)$ with energies between 37.5 and 45.5 kcal corresponding to $9 \leq v'' \leqq 11$. We adopt for (11) the rate coefficient

$$b_3 = 1.5 \times 10^{-12} T^{1/2} e^{-500/T} \quad \mathrm{cm^3\, sec^{-1}} \qquad (12)$$

The other reaction of nitric oxide with ozone [*Johnston and Crosby,* 1954] leads to ground state $\mathrm{NO_2}$ molecules

$$\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2} + 48\ \mathrm{kcal} \qquad (13)$$

with a rate coefficient [*Johnston and Crosby,* 1954; *Phillips and Schiff,* 1962a]

$$b_4 = 5 \times 10^{-14} T^{1/2} e^{-1200/T} \quad \mathrm{cm^3\, sec^{-1}} \qquad (14)$$

A chemiluminescent radiation [*Greaves and Garvin,* 1959] in the red and infrared ($\lambda >$ 5900 A) is emitted during reaction 13. It corresponds to an electronically excited state with a rate coefficient [*Clyne et al.,* 1964]

$$b_{4a} = 5 \times 10^{-14} T^{1/2} e^{-2100/T} \quad \mathrm{cm^3\, sec^{-1}} \qquad (14a)$$

In addition to these processes involving $\mathrm{NO_2}$, the following photodissociation process occurs in a sunlit atmosphere:

$$\mathrm{NO_2} + h\nu(\lambda < 3975) \rightarrow \mathrm{NO} + \mathrm{O} \qquad (15)$$

with the average photodissociation coefficient [*Bates,* 1954; *Leighton,* 1961]

$$J_{\mathrm{NO_2}} = 5 \times 10^{-3} \quad \mathrm{sec^{-1}} \qquad (16)$$

Under laboratory conditions the photolysis of nitrogen dioxide must involve an analysis [*Ford,* 1960] of $\mathrm{NO_3}$, $\mathrm{N_2O_5}$, etc. However, if a reaction such as $\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_3} + \mathrm{O_2}$ has an activation energy of the order of 7 kcal, $\mathrm{NO_2}$ will be unaffected during the night. For daytime conditions, excluding $\mathrm{NO_3}$ which has a dissociation energy of only 50 kcal, aeronomic conditions essentially correspond to the NO-NO_2 system.

Neglecting reactions in which hydrogen and nitrogen atoms are involved, the differential equation related to NO_2 is written as

$$\frac{dn(NO_2)}{dt} + [b_3n(O) + J_{NO_2}]n(NO_2) = [b_2n(O) + b_4n(O_3)]n(NO) \quad (17)$$

where $b_2 = b_{2a}n(M) + b_{2b}$. For daytime conditions an equilibrium exists, since

$$\tau_{NO_2} \leq 200 \text{ sec}$$

and

$$\frac{n(NO_2)}{n(NO)} = \frac{[b_{2a}n(M) + b_{2b}]n(O) + b_4n(O_3)}{J_{NO_2} + b_3n(O)} \quad (18)$$

Figure 1 is an illustration of the vertical distribution of the ratio $n(NO_2)/n(NO)$ which shows that, above the stratopause, nitrogen dioxide can be neglected in the analysis of nitric oxide reactions.

After twilight, when atomic oxygen is rapidly removed in the stratosphere by its association with molecular oxygen, the major process is, according to (17),

$$\frac{dn(NO_2)}{dt} = -\frac{dn(NO)}{dt} = b_4n(O_3)n(NO) \quad (19)$$

The lifetime of NO is very short during the night in the stratosphere, since $b_4n(O_3) > 3 \times 10^{-4}$ sec^{-1} (see Figure 1). In other words, nitric oxide disappears during dark hours in atmospheric regions where ozone is present in sufficient abundance.

In the upper mesosphere and thermosphere where $n(O)$ does not vary appreciably, the differential equation 17 with $J_{NO_2} = 0$ and $b_3n(O) > b_4n(O_3)$ indicates that the ratio $n(NO_2)/n(NO)$ increases after sunset as follows:

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2}{b_3}[1 - e^{-b_3n(O)t}] \quad (20)$$

Nighttime equilibrium conditions are reached very rapidly in the thermosphere but do not differ from daytime conditions (see Figure 1). The curves of Figure 1 show that the ratio $n(NO_2)/n(NO)$ shows the greatest change in the middle mesosphere where it depends on the rapidly varying concentrations of O_3 and O after sunset.

Finally, in the stratosphere below 30 km where the photoaction plays a role, the ratio $n(NO_2)/n(NO)$ increases and may correspond to a greater NO_2 concentration than that of NO, depending on the O_3 concentration.

Nitric oxide and atomic nitrogen. To deter-

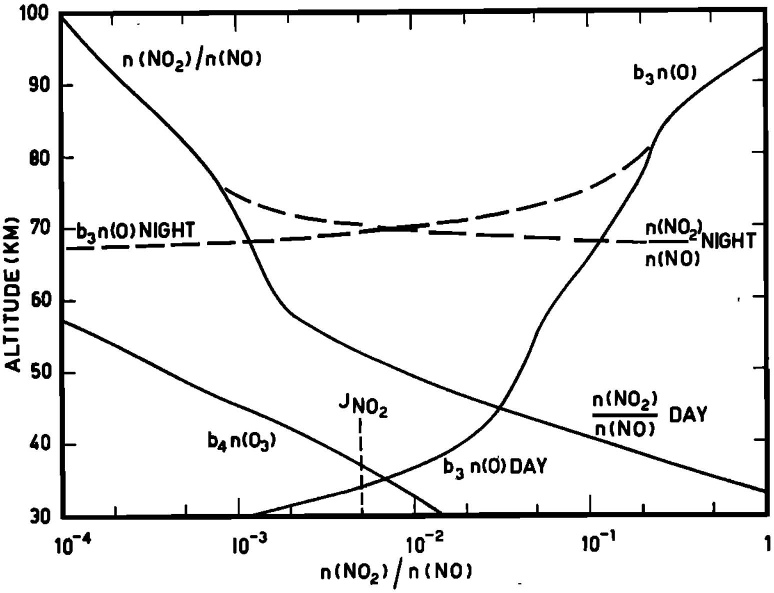

Fig. 1. Vertical distribution of the nitrogen dioxide and nitric oxide ratio of night and daytime equilibrium conditions. Note the action of atomic oxygen, $b_3n(O)$, and of ozone, $b_4n(O_3)$ sec^{-1}.

mine the behavior of nitric oxide, it is necessary to examine aeronomic reactions in which atomic nitrogen is effectively involved. In addition to (1) and (3), nitrogen atoms can react with nitrogen dioxide [*Kistiakowsky and Volpi,* 1957; *Harteck and Dondes,* 1958; *Kaufman and Kelso,* 1959; *Verbeke and Winkler,* 1960; *Clyne and Thrush,* 1961*d*].

$$N + NO_2 \rightarrow O + N_2O + 34 \text{ kcal} \qquad (21a)$$

$$\rightarrow NO + NO + 78 \text{ kcal} \qquad (21b)$$

$$\rightarrow N_2 + O_2 + 121 \text{ kcal} \qquad (21c)$$

for which a rate coefficient b_5 may be of the same order as for the other bimolecular reactions. However, while the reaction of atomic oxygen with nitrogen dioxide is more important in the aeronomic ratio $n(NO_2)/n(NO)$, the reactions of atomic nitrogen with nitric oxide and molecular oxygen are certainly the principal reactions in the chemosphere.

The following reaction [*Kistiakowsky and Volpi,* 1957; *Verbeke and Winkler,* 1960; *Herron,* 1961; *Clyne and Thrush,* 1961*a*; *Phillips and Schiff,* 1962*b*]

$$N + NO \rightarrow N_2 + O + 75 \text{ kcal} \qquad (22)$$

has a very small activation energy. We adopt the rate coefficient

$$b_6 = (1.5 \pm 0.5) \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \qquad (23)$$

which varies by about a factor of 2 between 200°K and 700°K. The fact that vibrational excitation [*Phillips and Schiff,* 1962*b*] of $N_2(v \leq 12)$ occurs in reaction 22 and may lead to a decomposition of ozone is of no practical aeronomic consequence. It can be shown that reaction 22 is not important in the stratosphere and lower mesosphere where atomic nitrogen does not exist. Such a reaction is, however, the most important nitrogen recombination process in the thermosphere.

The reaction of atomic nitrogen with molecular oxygen produces nitric oxide

$$N + O_2 \rightarrow NO + O + 32 \text{ kcal} \qquad (24)$$

with a maximum vibrational $NO(V = 6)$ excitation, and requires a relatively high activation energy [*Kistiakowsky and Volpi,* 1957; *Kaufman and Decker,* 1959; *Clyne and Thrush,* 1961*a*; *Mavroyannis and Winkler,* 1961*b*] of between 6 and 7 kcal. Laboratory determinations of the rate coefficient b_7 of (24) are fitted between 400°K and 1500°K by the expression

$$b_7 = 2 \times 10^{-13} T^{1/2} e^{-3000/T} \text{ cm}^3 \text{ sec}^{-1} \qquad (25)$$

which is adopted for the whole chemosphere. Such a rate coefficient is small at low mesospheric temperatures; nevertheless, it leads to an aeronomic production rate of NO molecules of about 10^{-5} sec^{-1} per nitrogen atom at the mesopause level and to about 10^{-3} sec^{-1} in the thermosphere.

Production of nitric oxide in the laboratory may also result from the reaction of nitrogen atoms with ozone [*Chen and Taylor,* 1961; *Phillips and Schiff,* 1962*a*].

$$N + O_3 \rightarrow NO + O_2 + 126 \text{ kcal} \qquad (26)$$

We adopt the rate coefficient

$$b_8 = 2 \times 10^{-12} T^{1/2} e^{-1200/T} \text{ cm}^3 \text{ sec}^{-1} \qquad (27)$$

This reaction would have an aeronomic role (only in the mesosphere) if nitrogen atoms were present in sufficient numbers. In fact, this reaction can be neglected, since the concentration of atomic nitrogen is small compared to that of atomic oxygen.

In addition to the loss process (equation 22) of nitric oxide occurring under day and nighttime conditions, it is necessary to add the following photodissociation process:

$$NO + h\nu(\lambda \sim 1900 \text{ A}) \rightarrow N + O \qquad (28)$$

for which *Bates* [1954] has adopted a rate coefficient at zero optical depth

$$J_{NO} = 10^{-7} \text{ sec}^{-1}$$

Furthermore, the photoionization of NO by Lyman α followed by dissociative recombination is also a loss process:

$$NO + h\nu(\lambda = 1216 \text{ A}) \rightarrow NO^+ + e \rightarrow N + O \qquad (29)$$

An average value of about 4 ergs cm^{-2} sec^{-1} for solar Lyman α leads to a rate coefficient at zero optical depth of

$$I_{NO} = 5 \times 10^{-7} \text{ sec}^{-1} \qquad (30)$$

Under equilibrium conditions between nitrogen dioxide and nitric oxide, the rate of change of $n(NO)$ is given by the following equation:

$$\frac{dn(NO)}{dt} + n(NO)[I_{NO} + J_{NO} + b_6 n(N)]$$
$$= [b_1 n(O) + b_7 n(O_2)]n(N) \qquad (31)$$

Hence, writing $dn(NO)/dt = 0$ in (31), the ratio $n(NO)/n(N)$ is given by

$$\frac{n(NO)}{n(N)} = \frac{b_1 n(O) + b_7 n(O_2)}{I_{NO} + J_{NO} + b_6 n(N)} \qquad (32)$$

In this formula, $b_6\, n(N)$ is the important term in the denominator if $n(N) > 5 \times 10^4$ cm^{-3}. Ignoring I_{NO} and J_{NO}, the equilibrium value of nitric oxide $n^*(NO)$ is then

$$n^*(NO) = 10^{-1} e^{-3000/T} n(O_2) + 5 \times 10^{-7} n(O) \qquad (33)$$

The second term on the right is small compared with the first in the mesosphere as well as where the temperature is high in the thermosphere. It becomes important at the atomic oxygen density peak which occurs in the lower thermosphere. A concentration of oxygen atoms of the order of 2×10^{12} cm^{-3} leads to

$$n^*(NO) = 10^6 \quad \text{cm}^{-3} \qquad (34)$$

At the mesopause level with $T = 190$°K, equation 33 leads to

$$n^*(NO) = 6 \times 10^5 \quad \text{cm}^{-3} \qquad (35)$$

i.e., about 3×10^{-9} of the total concentration.

The time to reach an equilibrium according to (31) depends on the term $b_6\, n(N)$ and, if $n(N) > n(NO)$, all conditions are required to reach a perfect chemical equilibrium. At the mesopause level, an atomic nitrogen concentration of at least 10^6 cm^{-3} is required to apply strictly equilibrium conditions, which can be attained in less than one day. Consequently, the production of nitrogen atoms must be studied near the mesopause level before deducing the aeronomic behavior of nitric oxide.

If we write $I_{NO} + J_{NO} > b_6\, n(N)$, so that (32) becomes

$$\frac{n(NO)}{n(N)} = \frac{b_7 n(O_2)}{I_{NO} + J_{NO}} \qquad (36)$$

which is applicable to mesospheric conditions, we obtain a ratio $n(NO)/n(N)$ greater than unity and increasing downward.

Atomic nitrogen in the chemosphere. Using the set of reactions written above, we find the equation governing the rate of change of atomic nitrogen to be

$$\frac{dn(N)}{dt} + n(N)[b_1 n(O) + b_6 n(NO) + b_7 n(O_2)]$$
$$= n(NO)[J_{NO} + I_{NO}] + 2P(N) \qquad (37)$$

in which the last term on the right takes into account the various possibilities of atomic nitrogen production.

In the chemosphere, only the following predissociation process, considered by *Herzberg and Herzberg* [1948], can be introduced:

$$N_2 + h\nu(\lambda\lambda \sim 1200 \quad \text{to} \quad 1250 \text{ A})$$
$$\rightarrow N_2(a^1\Pi_g) \rightarrow N + N \qquad (38)$$

in which Lyman-Birge-Hopfield bands are involved: namely (7–0) at 1250 A, (8–0) at 1226 A, and (9–0) at 1205 A. The most penetrating radiation corresponds to 1226 A, for which the absorption cross section should be of the order of 5×10^{-19} cm^2. According to *Bates* [1954], an approximate value of the dissociation rate coefficient at zero optical depth should be about

$$J_{N_2} = 10^{-12} \quad \text{sec}^{-1} \qquad (39)$$

By adding (31) and (37), we obtain the proper expression for photochemical changes:

$$\tfrac{1}{2} d[n(NO) + n(N)]/dt + b_6 n(NO)n(N)$$
$$= n(N_2)J_{N_2} \qquad (40)$$

or for equilibrium conditions:

$$b_6 n(NO)n(N) = n(N_2)J_{N_2} \qquad (41)$$

For example, a round figure of $n(NO)$ being 10^6 cm^{-3} sec^{-1} near 100 km leads to $n(N) \geq 10^6$ cm^{-3}.

If we adopt the relations

$$n^*(NO) = \frac{b_1 n(O) + b_7 n(O_2)}{b_6} \qquad (42)$$

$$n^*(N_2) = \frac{P(N)}{b_1 n(O) + b_7 n(O_2)} \qquad (43)$$

for the solutions of (41), the actual value of $n(NO)$ is

$$n(NO) = n^*(NO)/[1 + 10^5/n^*(N)]^{1/2} \qquad (44)$$

At the mesopause level the term $b_7\, n(O_2)$ is about 10^{-5} sec^{-1}, and any production of nitrogen atoms greater than 1 atom cm^{-3} sec^{-1} leads to a stationary value for n(NO), which is practically the equilibrium value n^*(NO).

In the mesosphere the loss of nitrogen atoms increases rapidly with decreasing height, and equilibrium conditions can always be applied to atomic nitrogen. Thus, assuming that only chemical changes occur, we have for the change of n(NO) in the mesosphere

$$\frac{dn(\mathrm{NO})}{dt} + 2b_6 n^2(\mathrm{NO}) \frac{I_{\mathrm{NO}} + J_{\mathrm{NO}}}{b_7 n(\mathrm{O}_2) + b_6 n(\mathrm{NO})}$$

$$= 2P(\mathrm{N})\left[\frac{b_7 n(\mathrm{O}_2) - b_6 n(\mathrm{NO})}{b_7 n(\mathrm{O}_2) + b_6 n(\mathrm{NO})}\right] \qquad (45)$$

Since $b_7\ n(\mathrm{O}_2)$ must be greater than $b_6\ n(\mathrm{NO})$, according to (42) and (44), the approximation

$$-\frac{dn(\mathrm{NO})}{dt} = 2b_6 \frac{I_{\mathrm{NO}} + J_{\mathrm{NO}}}{b_7 n(\mathrm{O}_2)} n^2(\mathrm{NO}) \qquad (46)$$

leads, by integration, to an approximate lifetime of nitric oxide in the mesosphere and lower atmospheric regions. The time τ_{NO} necessary to reduce the concentration n(NO) to 50% of its initial value n_0(NO) is

$$\tau_{\mathrm{NO}} = 10^6[n^*(\mathrm{NO})/n_0(\mathrm{NO})] \text{ sec} \qquad (47)$$

which is at least 10 days for any concentration less than the photochemical value defined by (42). Since n^*(NO) is certainly greater than the actual value n(NO) in the lower mesosphere, the possibility of maintaining nitric oxide in the mesosphere is real.

A photochemical value of $n(\mathrm{NO}) = 3 \times 10^{-9}$ n(M) at the mesopause with its extrapolation into the mesosphere, stratosphere, and troposphere leads to an acceptable concentration of nitrogen oxide at ground level [*Hutchinson*, 1954]. Considering the various ratios of $n(\mathrm{NO_2})/n(\mathrm{NO})$, as obtained by (18) and (20) and shown in Figure 1, it is possible to illustrate the vertical distributions of n(NO) and n(NO$_2$). Figures 2 and 3 show the variation in the stratosphere and mesosphere, respectively. Nitrogen dioxide and nitric oxide are of equal importance in the middle stratosphere around 30 km and, during the night, NO disappears by its transformation into NO$_2$. In the mesosphere there is a large variation between day and night. There is, furthermore, a transition zone corresponding to the region where atomic oxygen recombines after sunset. Above the mesopause, NO again increases and reaches a concentration in the *E* layer of about 10^6 cm^{-3}. Nevertheless, ionic reactions must be introduced in the ionosphere, and the numerical values given cannot be considered real in the ionospheric regions. Such conditions will be discussed after an analysis of the ionization processes.

Nitrogen trioxide, tetroxide, and pentoxide. In the ozonosphere, the reaction

$$\mathrm{O_3 + NO_2 \rightarrow NO_3 + O_2} + 26 \text{ kcal} \qquad (48)$$

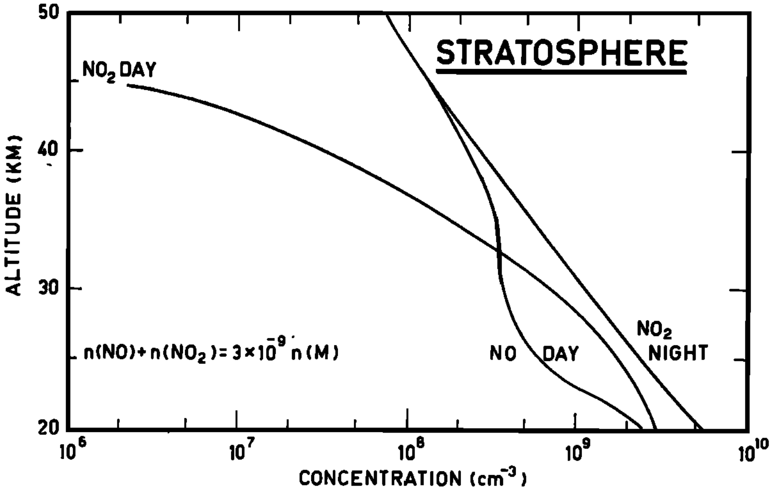

Fig. 2. Vertical distribution of nitric oxide and nitrogen dioxide in the stratosphere for day and nighttime conditions assuming a ratio $[n(\mathrm{NO}) + n(\mathrm{NO_2})]/n(\mathrm{M}) = 3 \times 10^{-9}$.

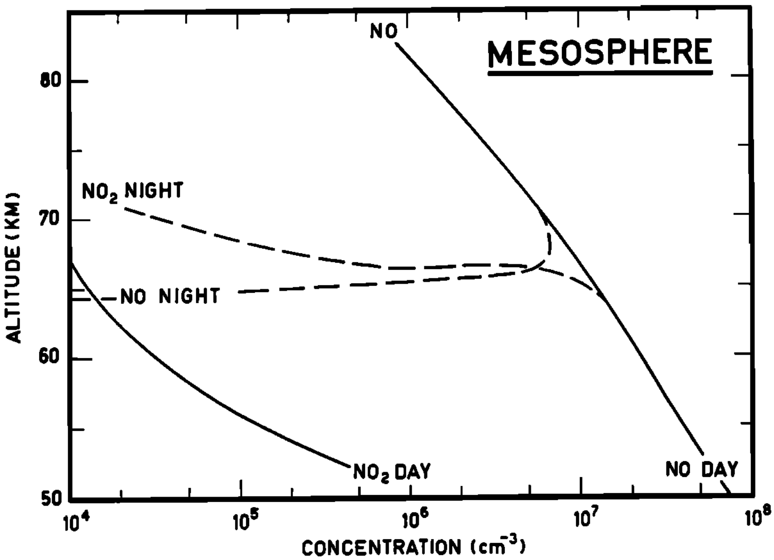

Fig. 3. Vertical distribution of nitric oxide and nitrogen dioxide in the mesosphere for chemical conditions without introducing the effect of ionospheric reactions; $n(\mathrm{NO})/n(\mathrm{M}) = 3 \times 10^{-9}$.

may occur. It has been studied in the laboratory [*Johnston and Yost,* 1949; *Ford et al.,* 1957; *Husain and Norrish,* 1963]. However, its activation energy (about 7 kcal) leads to a low rate coefficient b_9 in the stratosphere:

$$b_9 = 5 \times 10^{-13} T^{1/2} e^{-3600/T} \qquad (49)$$

Also, the three-body reaction

$$\mathrm{O} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{NO_3} + \mathrm{M} + 50\ \mathrm{kcal} \qquad (50)$$

may occur in the region where atomic oxygen is present. Its rate coefficient, b_{10}, is higher [*Ford and Endow,* 1957] than ordinary three-body reactions and may be about

$$b_{10} = 5 \times 10^{-31}\ \mathrm{cm^6\,sec^{-1}} \qquad (51)$$

For daytime conditions such reactions are followed by the rapid reaction

$$\mathrm{NO} + \mathrm{NO_3} \rightarrow 2\mathrm{NO_2} + 22\ \mathrm{kcal} \qquad (52)$$

which has a very small activation energy and may have a rate coefficient b_{11} of about

$$b_{11} = 5 \times 10^{-13} T^{1/2} e^{-1000/T} \qquad (53)$$

The presence of $\mathrm{NO_3}$ can therefore be neglected in a sunlit atmosphere because of the presence of NO and a photodissociation process, since there is an absorption spectrum in the visible region [*Jones and Wulf,* 1937; *Husain and Norrish,* 1963]. The nighttime conditions are different in the stratosphere owing to the absence of nitric oxide. The following processes [*Ford,* 1960; *Benson,* 1960; *Leighton,* 1961] can be considered:

$$\mathrm{NO_3} + \mathrm{NO_2} \rightarrow \mathrm{N_2O_5} + 21\ \mathrm{kcal} \qquad (54)$$

$$\mathrm{NO_3} + \mathrm{NO_2} \rightarrow \mathrm{NO} + \mathrm{NO_2} + \mathrm{O_2} - 4\ \mathrm{kcal} \qquad (55)$$

$$\mathrm{NO_3} + \mathrm{NO_3} \rightarrow 2\ \mathrm{NO_2} + \mathrm{O_2} + 18\ \mathrm{kcal} \qquad (56)$$

for which the following, very approximate, rate coefficients are adopted, respectively:

$$b_{12} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \qquad (57)$$

$$b_{13} = 3 \times 10^{-14} T^{1/2} e^{-2000/T} \qquad (58)$$

$$b_{14} = 1.5 \times 10^{-13} T^{1/2} e^{-3600/T} \qquad (59)$$

Reactions 48 and 54 will result in a $\mathrm{NO_2}$ loss process for nighttime conditions. Since the rate coefficient of (48) decreases from about $1.7 \times 10^{-17}\ \mathrm{cm^3\,sec^{-1}}$ at the stratopause to 1.7×10^{-18} near 30 km, the production of nitrogen trioxide is very small during a night of twelve hours. As a result the nitrogen dioxide is not affected and the production of nitrogen pentoxide is relatively small for normal nighttime conditions. Nevertheless, the problem of nitrogen trioxide and pentoxide cannot be neglected during long nights. The three-body association leading to nitrogen tetroxide should be considered for nighttime conditions

$$NO_2 + NO_2 + M \rightarrow N_2O_4 + M + 15 \text{ kcal} \tag{60}$$

for which the rate coefficient b_{15} is small [*Clyne and Thrush,* 1962*a*]

$$b_{15} = 8 \times 10^{-34} \quad \text{cm}^6 \text{ sec}^{-1} \tag{61}$$

The effect of (60) must be considered at low altitudes for nighttime conditions.

Thus, the reactions involving nitrogen dioxide (and ozone), (48) and (60), which occur during nighttime conditions may contribute somewhat to a temporary disappearance of nitrogen oxide in the stratosphere and below.

Nitroxyl, nitrous acid, and nitric acid. The formation of nitroxyl and its loss are due to a catalytic action of nitric oxide or atomic hydrogen. Such a process should be considered in the mesosphere and lower thermosphere where H and NO are present.

The three-body process

$$H + NO + M \rightarrow HNO + M + 49 \text{ kcal} \tag{62}$$

has been the subject of recent laboratory studies, since an infrared spectrum was detected [*Cashion and Polanyi,* 1959]. Absorption and emission bands [*Dalby,* 1958; *Clement and Ramsay,* 1961; *Bancroft et al.,* 1962] have been analyzed, and process 62 has been investigated in detail [*Clyne and Thrush,* 1961*b*, 1962*b*; *Strausz and Grunning,* 1964; *Bulewicz and Sugden,* 1964]. Considering that (62) has a negative activation energy [*Clyne and Thrush,* 1961b], the following rate coefficient, b_{16}, is used:

$$b_{16} = 1 \times 10^{-32} e^{300/T} n(\text{M}) \quad \text{cm}^3 \text{ sec}^{-1} \tag{63}$$

The chemiluminescent reaction involving H + NO, namely

$$H + NO \rightarrow HNO + h\nu \ (\lambda 7625\text{–}6925\text{–}7965\text{–}6272) \tag{64}$$

is slow [*Clyne and Thrush,* 1962*b*]. The rate coefficient is about

$$b_{16a} = 7 \times 10^{-19} (273/T)^3 \quad \text{cm}^3 \text{ sec}^{-1} \tag{65}$$

and process 64 is therefore unimportant in aeronomy.

The catalytic action of nitric oxide occurs in the recombination of hydrogen atoms; the bimolecular process [*Clyne and Thrush,* 1962*b*; *Bulewicz and Sugden,* 1964]

$$H + HNO \rightarrow NO + H_2 + 55 \text{ kcal} \tag{66}$$

having a small activation energy, has a rate coefficient b_{17} of the order of

$$b_{17} = 5 \times 10^{-13} T^{1/2} e^{-1200/T} \tag{67}$$

In a hydrogen-oxygen atmosphere, the action of OH and HO_2 must also be considered; the catalytic action of NO leads to

$$OH + HNO \rightarrow NO + H_2O + 69 \text{ kcal} \tag{68}$$

which has a larger rate coefficient [*Bulewicz and Sugden,* 1964] at flame temperature than reaction 66. We adopt the value

$$b_{18} = 5 \times 10^{-12} T^{1/2} e^{-1200/T} \tag{69}$$

which is about 10 times b_{17}.

The reaction

$$HO_2 + HNO \rightarrow NO + H_2O_2 + 40 \text{ kcal} \tag{70}$$

should also occur, but its rate coefficient b_{20} is not known. We consider that

$$b_{17} \leq b_{20} \leq b_{18} \tag{71}$$

The net result of reactions 62 to 70 is that nitric oxide is not affected. Atomic hydrogen is subject to other more important loss processes, and its chemiluminescent reaction in the formation of nitroxyl is not important.

The possible three-body associations leading to nitrous and nitric acids

$$NO_2 + H + M \rightarrow HNO_2 + M + 80 \text{ kcal} \tag{72}$$

$$NO + OH + M \rightarrow HNO_2 + M + 60 \text{ kcal} \tag{73}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M + 53 \text{ kcal} \tag{74}$$

$$NO + HO_2 + M \rightarrow HNO_3 + M + 63 \text{ kcal} \tag{75}$$

with the respective rate coefficients b_{20}, b_{21}, b_{22}, and b_{23} (which are not known) should be compared with the reactions

$$HNO_2 + H \rightarrow H_2 + NO_2 + 23\ \text{kcal} \qquad (76)$$

$$HNO_2 + OH \rightarrow H_2O + NO_2 + 38\ \text{kcal} \qquad (77)$$

$$HNO_3 + H \rightarrow H_2O + NO_2 + 66\ \text{kcal} \qquad (78)$$

$$HNO_3 + H \rightarrow H_2O + NO_3 + 15\ \text{kcal} \qquad (79)$$

which are exothermic reactions for which the activation energies likewise are not known. Their respective rate coefficients b_{24}, b_{25}, b_{26}, and b_{27} should be very small if HNO_2 and HNO_3 have some importance. In any case, NO_2 has a catalytic action, and the nitrogen oxides are not affected by reactions 72 to 79. The loss processes of H, OH, and HO_2 are not important compared with other processes in which O, O_2, and O_3 are involved.

Finally, three other reactions in which nitrogen oxides are involved must be considered. The presence of NO_2 leads to a very rapid process [*Rosser and Wise,* 1961; *Clyne and Thrush,* 1961*c*; *Ashmore and Tyler,* 1962; *Phillips and Schiff,* 1962*d*; *Kaufman,* 1964] with practically no activation energy

$$H + NO_2 \rightarrow NO + OH + 30\ \text{kcal} \qquad (80)$$

with

$$b_{28} = 2 \times 10^{-12} T^{1/2} \qquad (81)$$

which corresponds to laboratory measurements [*Phillips and Schiff,* 1962*d*]. Such a reaction is, however, less important than the reaction $H + O_3 \rightarrow OH + O_2$, since $n(O_3) > n(NO_2)$. The role of (80) as an NO_2 loss process is also limited, since $O + NO_2 \rightarrow NO + O_2$ is the principal reaction.

The effect of NO on HO_2 and H_2O_2 is given by the reaction

$$NO + HO_2 \rightarrow OH + NO_2 + 9\ \text{kcal} \qquad (82)$$

which is fast relative to other reactions of HO_2 in similar circumstances [*Tyler,* 1962]. If an upper limit of about 2.5 kcal is assumed for the activation energy of a reaction such as $O_3 + NO \rightarrow O_2 + NO_2$ with a rather high pre-experimental factor, a rate coefficient b_{29} of about 10^{-11} $cm^3\ sec^{-1}$ at 500°K leads to

$$b_{29} = 5 \times 10^{-12} T^{1/2} e^{-1200/T} \qquad (83)$$

Under aeronomic conditions, such a reaction must be compared with the rapid reaction $HO_2 + O \rightarrow OH + O_2$ or with $NO + O_3$ and $NO + O$. Its aeronomic role is, therefore, not important. The reaction

$$NO + H_2O_2 \rightarrow HNO_2 + OH + 11\ \text{kcal} \qquad (84)$$

for which the rate coefficient b_{30} is not known can also be neglected, since $O + H_2O_2 \rightarrow H_2O + O_2$ has the leading role as a loss process of hydrogen peroxide under aeronomic conditions.

Summary. The essential reactions in which nitrogen oxides are involved in the chemosphere depend on atomic oxygen and ozone. The hydrogen compounds do not play an important role, and all their reactions with NO and NO_2 can be neglected. The processes affecting the ratio $n(NO_2)/n(NO)$ are essentially described by (17) and (18) in which only three reactions involving atomic oxygen, and ozone with the photodissociation of NO_2, describe the aeronomic conditions.

The absolute values of NO and NO_2 depend on the dissociation of N_2 in the lower thermosphere. Since the lifetime of nitric oxide in the mesosphere is relatively long, any downward transport leads to a vertical distribution of NO which follows the hydrostatic distribution. In view of the fact that the chemical reactions occur in the ionosphere and that a chemospheric hypothesis for nitric oxide does not hold there, as will be shown in another paper, it is necessary to introduce other indirect processes for the dissociation of molecular nitrogen.

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