Nitrogen oxides and the airglow

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ABSTRACT

The chemospheric processes lead to various possibilities for description of the contribution of nitrogen oxides in the airglow. An excitation of the Vegard-Kaplan system is indicated when nitric oxide is formed by a three-body collision process involving molecular nitrogen. A bimolecular association leading to nitrogen peroxide must show a continuous airglow during dark hours as well as in a sunlit atmosphere. Electronic systems emission of NO_2 is also possible because of a reaction between ozone and nitric oxide.

A reaction leading to an excitation of the O_2 red atmospheric band system with its peculiar emissions is also discussed.

Since these various processes causing day, twilight, and night airglow occur in the mesosphere and at the mesopause level, dynamic effects may lead to strong variations in the airglow.
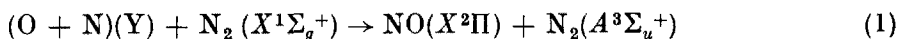
1. Introduction

THE study of the identification of the airglow radiations suggests that additional processes are required to explain ultraviolet and visible features. Using results obtained in a preceding paper (NICOLET, 1955), we discuss various possibilities here that may be of importance in the airglow. Before accepting a high-altitude origin for all of the emissions of the airglow, it is necessary to assess the likelihood of occurrence of some chemical reactions; and, in particular, the contributions of the nitrogen oxides have to be studied. An initial study, made by BATES (1952, 1954) and BATES and WITHERSPOON (1952), has led to our brief analysis of the aeronomic problem of nitrogen oxides (NICOLET, 1955) in which several reactions involving atomic oxygen and ozone were discussed. It appears that the main processes thus far discussed can provide possible mechanisms of excitation for the airglow.
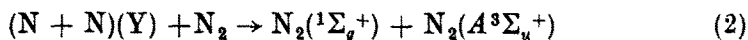
2. Nitric Oxide Formation and the Vegard-Kaplan System

It does not appear possible to accept the previous identifications of night-airglow radiations with the Vegard-Kaplan intercombination system of N_2. However, bands which seem to show a degradation toward the red lead, as may be expected from synthetic spectra, to the possibility that some night-airglow emissions would be due to a relatively small number of these N_2 bands.

In the thermosphere, the presence of nitrogen and oxygen atoms results in the formation of nitric oxide. It is interesting to consider the following mechanism:

$$(O + N)(Y) + N_2 (X^1\Sigma_g^+) \rightarrow NO(X^2\Pi) + N_2(A^3\Sigma_u^+) \tag{1}$$

instead of the reaction usually invoked:

$$(N + N)(Y) + N_2 \rightarrow N_2(^1\Sigma_g{}^+) + N_2(A\,^3\Sigma_u{}^+) \tag{2}$$

for the excitation of the Vegard-Kaplan bands.

BATES (1952) has discussed the process of type (2) and shown that it is not able to give an observable intensity of Vegard-Kaplan band-system emission unless the nitrogen-atom concentration is considerable.

With (1), the presence of oxygen atoms is of interest, since it increases the the rate of the process. Nevertheless, other objections can be made, such as those BATES (1952) has indicated. It seems, however, that the conditions are less severe with (1) than with (2); and a limited excitation is to be expected.

If an effort is made toward finding a possible mechanism for the excitation of Vegard-Kaplan bands in the night airglow, attention may be drawn to the fact that (1) is energetically possible. The dissociation energy of nitric oxide is about 150 kcal (GAYDON, 1947; BRIX and HERZBERG, 1954), while the excitation energies of $N_2(A\,^3\Sigma)$ are as follows:

$$v' = 0 \quad 142\cdot2 \text{ kcal}$$
$$v' = 1 \quad 146\cdot3 \text{ kcal}$$
$$v' = 2 \quad 150\cdot3 \text{ kcal}$$

Adopting the conditions BATES (1952) has chosen for (2), $n(N)$ would have smaller values using (1). Instead of 10^{11} cm^{-3}, for example, about 6×10^8 nitrogen atoms would be needed.

For the formation of NO we may write

$$\frac{dn(\text{NO})}{dt} = 5 \times 10^{-34} T^{1/2} n(\text{M}) n(\text{O}) n(\text{N}) \tag{3}$$

in which the rate coefficient has chosen to be the same as for the formation of O_2 by three-body collisions (BATES and NICOLET, 1950).

The excitation from $^1\Sigma$ to $A\,^3\Sigma(v' \leq 2)$ of N_2 will be

$$\frac{dn(N_2, A\,^3\Sigma)}{dt} = 4 \times 10^{-34} T^{1/2} n(N_2) n(\text{O}) n(\text{N}) p_{12} \tag{4}$$

in which p_{12} denotes the probability factor for the excitation, and $n(N_2) = \frac{4}{5} n(\text{M})$.

The emission from $A\,^3\Sigma$ to $A\,^1\Sigma$ will be

$$\frac{dn(VK)}{dt} = p_{12} p_{21}\, 4 \times 10^{-34} T^{1/2} n(N_2) n(\text{O}) n(\text{N}) \tag{5}$$

in which p_{21} denotes the probability factor for the deactivation.

At 120 km, a yield for the total emission in the Vegard-Kaplan bands of the order of 10 cm^{-3} sec^{-1} requires a concentration of nitrogen atoms of about 2×10^8 cm^{-3} if $p_{12} p_{21} = 1$.

With the same conditions ($p_{12} p_{21} = 1$), and keeping the day concentration of oxygen atoms, it is possible to reach the same yield with 2×10^6 nitrogen atoms cm^{-3} at 50 km and 2×10^7 cm^{-3} at 80 km.

In other words, the presence of Vegard-Kaplan bands would be detected in airglow spectra if $p_{12}p_{21} = 1$ and, therefore, the emission would be more important at mesospheric levels than in the thermosphere. However, as deactivation must occur,

$$p_{21} \ll 1 \qquad (6)$$

and p_{21} increases towards low altitudes. From 120 km to 50 km, the variation of the factor p_{21} should be more than 10^4; for example,

$$p_{21}^{(120\,\text{km})} : p_{21}^{(90\,\text{km})} : p_{21}^{(55\,\text{km})} = 1 : 10^{-2} : 10^{-4} \qquad (7)$$

The detection of Vegard-Kaplan bands in airglow spectra requires:

(i) an atomic nitrogen concentration not less than $10^8\,\text{cm}^{-3}$;

(ii) a complete excitation in the association process (1); and

(iii) no deactivation effect.

Therefore, there is maximum probability of the emission in the thermosphere where $n(\text{O})n(\text{N})$ is maximum. However, the exact rate of such an emission cannot be determined without knowledge of the deactivation factor. In any case, the emission rate should be less than $10\,\text{cm}^{-3}\,\text{sec}^{-1}$, and the observation of Vegard-Kaplan bands, even if possible, should be difficult. Because of a deactivation effect, the final possibility is the emission of bands from $A^3\Sigma$ ($v' = 0$).

3. Nitrogen Peroxide and the Atmospheric Oxygen System

If the concentration of NO_2 is sufficiently large, the following process may be considered for an excitation of O_2,

$$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2, \qquad (8)$$

for which the rate coefficient b_3 is not well known at mesospheric temperatures (Nicolet, 1955).

According to data deduced from the chemical equilibrium, $\text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2$, the dissociation energy of NO_2 is about 72 kcal. The data of Bodenstein and Lindner (1922), considered by Zeise (1936), lead to

$$E_0^0 = -25\cdot55\,\text{kcal} = 2D_0^0(\text{NO}) + D_0^0(\text{O}_2) - 2D_0^0(\text{NO}_2) \qquad (9)$$

in which E_0^0 is the heat of reaction at 0°K and D_0^0 the atomic heats of formation (or the heat of dissociation for diatomic molecules).

Since the heat of dissociation of O_2 is $117\cdot96$ kcal (Brix and Herzberg, 1954), the following equation can be written,

$$\text{NO}_2 = \text{NO} + \text{O} + 71\cdot75\,\text{kcal}. \qquad (10)$$

The photochemical decomposition is complete at $\lambda3650$ Å (Hg line), while at $\lambda4050$ Å (Hg line) the efficiency is not complete (predissociation?), and at $\lambda4360$ Å no detectable effect was found (Norrish, 1929; Holmes and Daniels, 1934). According to Noyes and Leighton (1941), excited molecules are produced by $\lambda > 3700$ Å, and a few of these may be expected to dissociate by acquisition of thermal energy. The predissociation has been considered (Herzberg, 1931;

NOYES and HENRIQUES, 1939); however, it is difficult to determine a precise value of the dissociation energy of NO_2, since that for thermal decomposition is only an average value. It may be pointed out that HALL and BLACETT (1952), having separated the absorption spectra of NO_2 and N_2O_4, indicate an effect of the NO_2 spectrum at 3900 Å which could alter the photochemistry of the system.

In any case, it appears that the energy of dissociation of NO_2 into $NO + O$ cannot be greater than 77 kcal, and is probably near 72 kcal. Considering (8), the excitation of O_2 may correspond to

$$NO_2 + O \rightarrow NO + O_2(^1\Sigma, v' \leq 2) \tag{11}$$
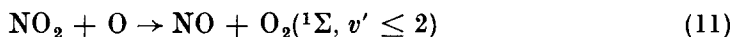
i.e., to an excitation at $v' \leq 2$ for the lowest value of the NO_2 dissociation energy and $v' = 0$ for the largest value.

In order to explain an emission from $O_2(^1\Sigma, v' = 0)$ alone, as is observed in the airglow, when $D(NO_2) = 72$ kcal, it is necessary to suppose that resonance is not effective or to introduce BATES's process (1954), in which the vibrational energy is transformed by collision to the zeroth vibrational level of the excited electronic state.

Because of the uncertainty of the coefficient values, it is not possible to determine the exact rate of (11). However, by using extreme values for (11) (NICOLET, 1955), we may obtain estimates as follows:

At 200°K, with $n(NO_2) = 10^7$ cm^{-3}, a yield of 50 photons cm^{-3} sec^{-1} in the atmospheric bands of O_2 requires an atomic oxygen concentration between 10^{11} and 4×10^{10} cm^{-3}. At mesospheric levels, the reaction rates of (11) would be of the order of 10^{-5} cm^{-3} sec^{-1} to 5×10^{-5} cm^{-3} sec^{-1} between 80 km and 90 km. Therefore a total rate of $2 \cdot 5 \times 10^8$ photons cm^{-2} sec^{-1} needs only an average concentration $n(NO_2) = 10^7$ cm^{-3}. Since such a value can be reached after twilight (NICOLET, 1955), process (11) does exist, and leads to an emission which must be variable according to the mesospheric conditions.

Finally, it is interesting to notice that KAPLAN (1952) was the first to observe the atmospheric bands in oxygen afterglows containing small amounts of nitrogen. These afterglows are much more intense than those observed in pure oxygen. There is strong emission in the visible and in the photographic infrared due to NO_2.

4. NITROGEN PEROXIDE AND AFTERGLOW

The radiative process

$$O + NO \rightarrow NO_2 + h\nu \tag{12}$$

has been studied in the laboratory by a number of investigators (RAYLEIGH, 1910; STODDARD, 1934; NEWMAN, 1935; SPEALMAN and RODEBUSH, 1935; GAYDON, 1944; TANAKA and SHIMAZU, 1948). Other investigations are those of NORRISH (1929) and BAXTER (1930) pertaining to fluorescence, and of KONDRATJEW (1937) concerning the thermal radiation of nitrogen peroxide. They also show that the general spectrum may be considered as a continuous spectrum with a possible banded structure.

Let us first discuss the bimolecular association (12), which corresponds to the continuous afterglow found by RAYLEIGH (1910) from about 4200 Å to 6700 Å,

and observed in more detail by STODDARD (1934) and NEWMAN (1935) in a discharge through air or through oxygen with traces of nitrogen. The similarity of the colours of this afterglow and the emission of flames containing oxides of nitrogen (GAYDON, 1944) indicate that process (12) is an important one.

TANAKA and SHIMAZU (1948) have observed the chemiluminescence in the reactions between nitric oxide and oxygen and ozone, using discharges through air, NO, NO_2, and mixed gas. They have found various afterglows indicating that NO is necessary, and O_3 is perhaps not essential.

Adopting the value of 10^{-17} cm^{-3} sec^{-1} for the rate coefficient of (12) (BATES, 1954), a yield of 10^3 photons cm^{-3} sec^{-1} at $\lambda \geq 3900$ Å would result from only 2×10^{11} oxygen atoms if we adopt 5×10^8 NO molecules per cm^3.

Considering the possible values of $n(NO) \geq 10^8$ cm^{-3} (NICOLET, 1955), there is no doubt that (12) may produce a continuous airglow spectrum, for the rate of (12) between 80–90 km is of the order of $2 \times 10^{-6} n(NO)$ cm^{-3} sec^{-1}. A total continuous emission of more than 10^9 photons ($\lambda \geq 3900$ Å) per cm^2 and sec can be obtained in the night airglow.

As has been shown (NICOLET, 1955), the bimolecular reaction involving ozone molecules leads to the excitation of NO_2,

$$O_3 + NO \to O_2 + NO_2, \tag{13}$$
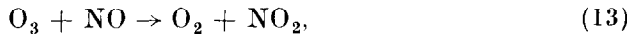
which corresponds to an energy of not less than 48 kcal. In other words, the energy released by this reaction is used for an excitation of NO_2 in an electronic level leading most certainly to an emission of bands at $\lambda > 5950$ Å. Since we know that the visible oxygen afterglow also consists of bands, for example at $\lambda\lambda 5980$–6320–6400 Å, it is possible to consider an airglow spectrum having such a behaviour. This conclusion can be used to explain the experimental results of TANAKA and SHIMAZU (1948). Furthermore, it is interesting to note that the observed airglow seems to show a diffuse spectrum in the region of the sodium and red oxygen lines.

The activation energy of (13) being very low, the rate coefficient is large. In the mesosphere, at 65 km for example, where a value of more than 10^9 O_3 molecules cm^{-3} and a temperature of the order of 250°K may be adopted, the rate of formation of NO_2 by (13) would be of the order of

$$\frac{dn(NO_2)}{dt} \geq 10^{-5} n(NO) \text{ cm}^{-3}\text{-sec}^{-1}. \tag{14}$$

Considering a possible concentration for $n(NO)$ of 10^9 cm^{-3} sec^{-1}, the rate of excitation in (14) would be of the order of 10^4 cm^{-3} sec^{-1}.

This process will be efficient during twilight, and it must therefore be considered as playing a disturbing role in the twilight emissions as observed in the red lines of atomic oxygen and even, perhaps, for the sodium line.

As was shown in a preceding paper (NICOLET, 1955), all the reactions discussed here are very sensitive to the concentrations adopted, and depend on the activation energy chosen for (11). If chemical data were more precise, it would be possible to discuss in a more quantitative manner the diurnal variation of nitrogen oxide concentrations.

These various results on the possible effects of nitrogen oxides in the night airglow may be related with observational data. For example, the continuum of the airglow spectrum, starting at about 3900 Å, should be affected by these reactions even if the major part is due to a stellar continuum (CHAMBERLAIN and OLIVER, 1953; MEINEL, 1953).

5. DAY AIRGLOW

Observational data obtained by rocketborne photoelectric photometers (MILEY, CULLINGTON, and BEDINGER, 1952) have been discussed recently by BATES and DALGARNO (1954). After this analysis, it is interesting to make an attempt to describe the behaviour of nitrogen oxides in the day airglow.
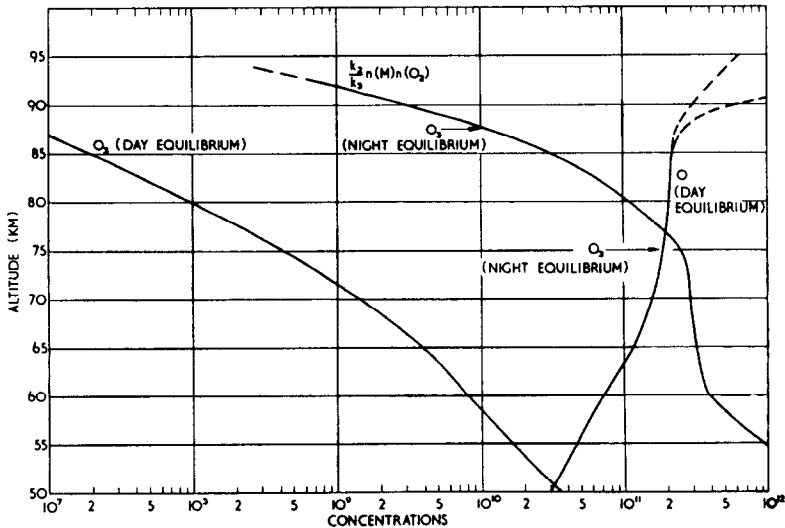

Fig. 1. Concentrations of ozone and atomic oxygen in an atmosphere in which the effect of minor constituents is neglected.

To make the position clear, the vertical distributions of ozone and atomic oxygen between 50 km and 90 km are given in Fig. 1. The atomic oxygen concentration is greater than the ozone concentration under daytime photoequilibrium conditions. At any time during the day, the photoequilibrium does exist for ozone. During dark hours, the problem is entirely different, and is not studied here. It must be pointed out that the night-time distribution shown in Fig. 1 deals with night-time equilibrium values in an oxygen atmosphere. Insofar as atomic oxygen is concerned, the problem of photoequilibrium is different. In Fig. 2 various states of recombination are shown. The upper curve corresponds to the loss-rate coefficient of oxygen atoms by association with O_2. The lower curve corresponds to a recombination effect by reaction between O and O_3 in a sunlit atmosphere. The right heavy curve represents the same process with the maximum possibility during hours of darkness. The heavy curve in the left part of that figure shows the effect of the recombination of two oxygen atoms. This effect becomes preponderant above 85 km. Furthermore, the surface limited

by the heavy curves shows the possible limits for the recombination of oxygen atoms in an oxygen atmosphere. It indicates that below 60 km the time of recombination is less than one day. At 75 km the minimum time is obtained during dark hours and is of the order of twenty-four hours. At 80 km, this minimum time is of the order of three days.

In view of the above, we cannot increase the oxygen concentration below 65 km by vertical transport, for the recombination by collision between O_3 and O is effective in less than one hour for $n_0(O) = 3 \times 10^{11}$ cm^{-3} But from 65 to 75 km the concentration of 2×10^{11} cm^{-3} may have a lifetime of not less than three hours. Thus, it may be concluded that the vertical transport of oxygen atoms to lower heights is possible. Above 80 km, we may have a concentration of oxygen
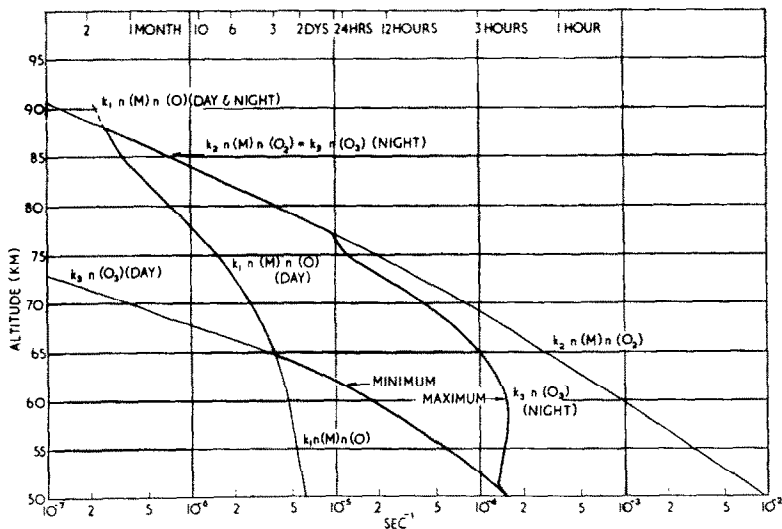

Fig. 2. Recombination rate coefficients of oxygen atoms versus height or lifetimes of oxygen atoms.

atoms larger than the photochemical value, because the time of dissociation is longer than two days.

At 90 km, the process which plays an effective role in the recombination of oxygen is the normal association of oxygen by a three-body collision.

The aeronomic problem is more complicated than the problem in an oxygen atmosphere. It was shown by BATES and NICOLET (1950) that the presence of hydrogen may affect the general behaviour. However, the aeronomic study of nitrogen oxides (NICOLET, 1955) shows difficulties such that preliminary conclusions are hardly changed by use of an oxygen atmosphere.

In any case, the assignment of a night-airglow spectrum to reactions between nitric oxide and atomic oxygen or ozone, and between nitrogen peroxide and oxygen, suggests possible effects resulting in an important day airglow.

In a sunlit atmosphere, process (12) attains its maximum rate, since $n(NO)$ and $n(O)$ certainly have their maximum values under these conditions. When
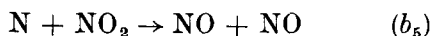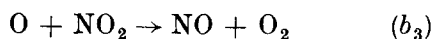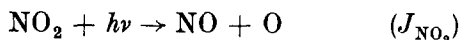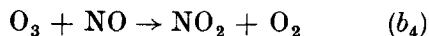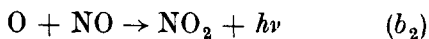
NO$_2$ is produced by (12), this molecule emits its continuous spectrum and, afterwards, is dissociated after a mean lifetime of 200 seconds (Bates, 1954). But before dissociating, NO$_2$ can be excited to an excited electronic level from which fluorescence occurs. This last process was observed in the laboratory (Norrish, 1929; Baxter, 1930) when there were recognized two characteristic bands lying in the red-orange and yellow-green regions, namely broad bands between 6200–6500 Å and 5600–6050 Å. Baxter (1930) has assumed a mean lifetime of the electronic state of the order of 10^{-7} sec, and Heil (1932) has obtained a time of about 10^{-5} sec by a diffusion method. Since the absorption coefficient of NO$_2$ has a peak near 4000 Å (Hall and Blacett, 1952) of the order of 10^{-18} cm^2, and is still about 7×10^{-19} cm^2 at 5000 Å, in a spectral region where the solar emission is most important, it seems, therefore, that an absorption process leading to an excitation giving fluorescence is not less effective than a photodissociation process due to the ultraviolet radiation. In other words, during its lifetime of 200 seconds, nitrogen peroxide can be excited to an electronic level to emit a fluorescence spectrum. Unfortunately, the experimental data are not suitable for theoretical determinations. The recent analysis of Neuberger and Duncan (1954) shows that the fluorescence spectrum of NO$_2$ excited by $\lambda 4358$ Å is apparently continuous at low dispersion, and extends from the exciting line to the limit of observation at about 8000 Å. The fluorescence spectrum excited by a radiation of longer wavelength, namely $\lambda 5461$ Å, shows relatively sharp emission bands superimposed on an apparently continuous emission. Since the interpretation of such experimental data is difficult (the knowledge of the electronic levels of NO$_2$ being very poor), no simple suggestion can be offered; the fluorescence spectrum due to relatively short wavelengths must be ascribed to a series of different levels which partly overlap. However, the narrow bands obtained by the excitation of $\lambda 5461$ Å may be of importance in the day airglow. These bands have the following approximate wavelengths: $\lambda\lambda 5890, 6160, 6385, 6460, 6540$, and 6700 Å. They come from electronic levels having a very short lifetime ($\sim 10^{-7}$ sec), and cannot be excluded from twilight phenomena. A certain number of features observed in twilight spectra which are not due to OH emissions may belong to NO$_2$. As far as the apparently continuous spectrum is concerned, its lifetime is relatively long and is of the order of 4.4×10^{-5} sec, according to Neuberger and Duncan (1954). Without any additional contribution toward the interpretation of this spectrum it is not possible to reach a more precise conclusion concerning the fluorescence of the day or twilight airglow.

The whole problem is complicated, for it is a problem of radiation transfer involving absorption of solar radiation by NO$_2$, eventual fluorescence after collisions at low height, photodissociation, and, perhaps, subsequent absorption. Nevertheless, the way in which nitrogen oxides and their various reactions may behave in the day airglow must be shown.

Let us consider the photoequilibrium which does exist between NO$_2$ and NO. The equation of photoequilibrium is (see Nicolet 1955, equation (18)),

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_2 n(\text{O}) + b_4 n(\text{O}_3)}{J_{\text{NO}_2} + b_3 n(\text{O}) + b_5 n(\text{N})} \tag{15}$$

in which the rate coefficients correspond to the following reactions

$$O + NO \rightarrow NO_2 + h\nu \qquad (b_2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (b_4)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (J_{NO_2})$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (b_3)$$

$$N + NO_2 \rightarrow NO + NO \qquad (b_5)$$

Inserting numerical values in (15), the ratio $n(NO_2)/n(NO)$ for day equilibrium has been found and is shown in Fig. 3. It is less than unity in the atmospheric region which was analyzed, and decreases with increasing heights.
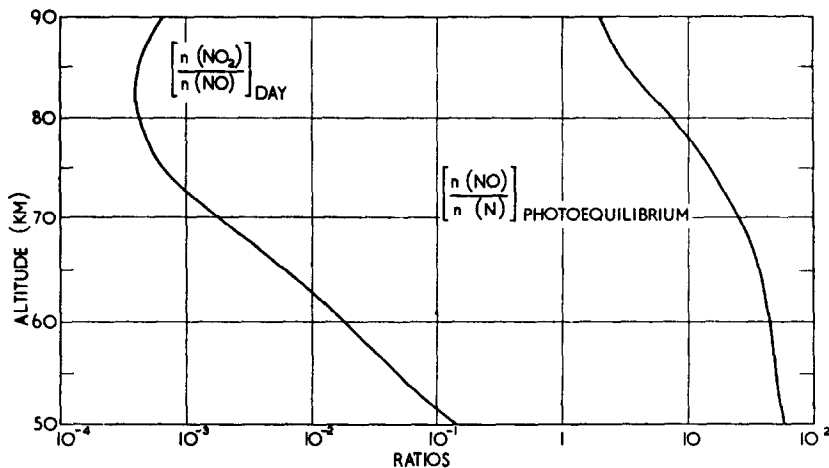

Fig. 3. Photoequilibrium conditions. $n(NO_2)/n(NO)$ corresponding to real conditions. $n(NO)/n(N)$ for a limiting case, since departure from photoequilibrium conditions does exist.

Using the complete set of reactions, the equation governing the rate of change of $n(NO)$ is (see NICOLET, 1952, equation (32)).

$$\frac{dn(NO)}{dt} = b_1 n(M) n(O) n(N) - \left[J_{NO} + b_6 n(N) \right] n(NO) \qquad (16)$$

in which the rate coefficients correspond to the following reactions:

$$O + N + M \rightarrow NO + M \qquad (b_1)$$

$$NO + h\nu \rightarrow N + O \qquad (J_{NO})$$

$$NO + N \rightarrow N_2 + O \qquad (b_6)$$
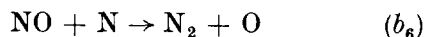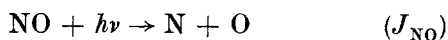
It is not possible to find the variation of $n(NO)$ from equation (16), because of its dependence on the atomic nitrogen concentration. Furthermore, photo-equilibrium cannot be accepted because of the long lifetime of NO and, since in any case, the lifetime of atomic nitrogen is more than one day. Nevertheless, by considering the ratio $n(NO)/n(N)$, which under equilibrium conditions depends on the association between oxygen and nitrogen atoms, it is possible to reach

preliminary conclusions using (16) in which $\dfrac{dn(\mathrm{NO})}{dt} = 0$. Such a hypothesis means that the variation of NO due to photodissociation is less rapid than the loss of nitrogen atoms entering into the formation of nitric oxide. We can assume such a process, for the mean lifetime of a nitrogen atom is of the order of $1 \cdot 5 \times 10^5$ sec at 50 km and $1 \cdot 3 \times 10^6$ sec at 75 km.
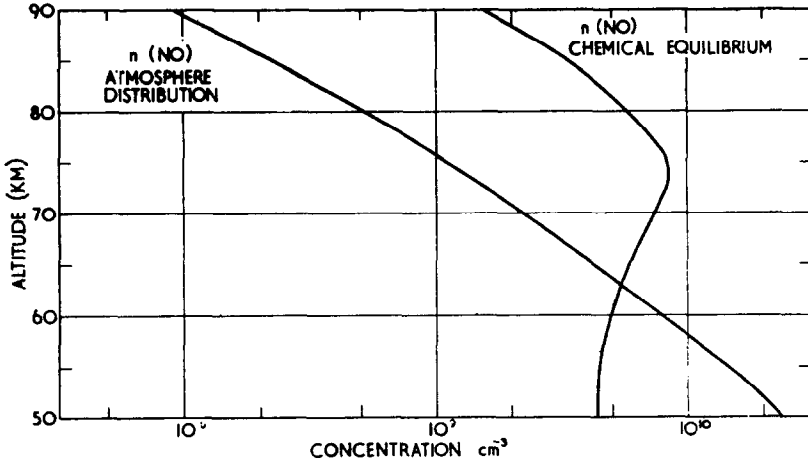

Fig. 4. Extreme cases of the vertical distribution of nitric oxide.

Since this behaviour implicitly assumes that $n(\mathrm{NO}) > n(\mathrm{N})$, which is correct below 90 km, we can write the following condition

$$J_{\mathrm{NO}} > b_6 n(\mathrm{N}), \tag{17}$$

and therefore

$$\frac{n(\mathrm{NO})}{n(\mathrm{N})} = \frac{b_1 n(\mathrm{M}) n(\mathrm{O})}{J_{\mathrm{NO}}} \tag{18}$$

corresponding to photochemical conditions. Using numerical values in (18), we find approximate results which show (Fig. 3) a decrease of the ratio $n(\mathrm{NO})/n(\mathrm{N})$ from about 50 near 50 km to unity above 90 km.

It is not possible to deduce the vertical distribution of $n(\mathrm{NO})$ from (16) or (18). However, utilizing a chemical equilibrium by employing the condition,

$$J_{\mathrm{NO}} < b_6 n(\mathrm{N}), \tag{19}$$

instead of (17), the following equation can be written,

$$n(\mathrm{NO}) = \frac{b_1}{b_6}\, n(\mathrm{M}) n(\mathrm{O}) \tag{20}$$

which leads to the vertical distribution of nitric oxide concentration shown in Fig. 4. Such a distribution corresponding to the limiting case of chemical equilibrium, does not correspond to aeronomic conditions, as has been shown (NICOLET, 1955); we must consider the problem of the departure from equilibrium conditions so far as nitric oxide is concerned. Taking an average value of 5×10^8 cm^{-3}

for the nitric oxide concentration at 80 km, a value which may be used to interpret the ionospheric behaviour of region D (NICOLET, 1955), it is possible to invoke mixing (complete departure from photochemical conditions) in order to adopt the atmospheric distribution for nitric oxide (Fig. 4).

In considering the content of a column of about 30 km between 50–90 km, one is permitted to use the same total number of molecules accurate to within one
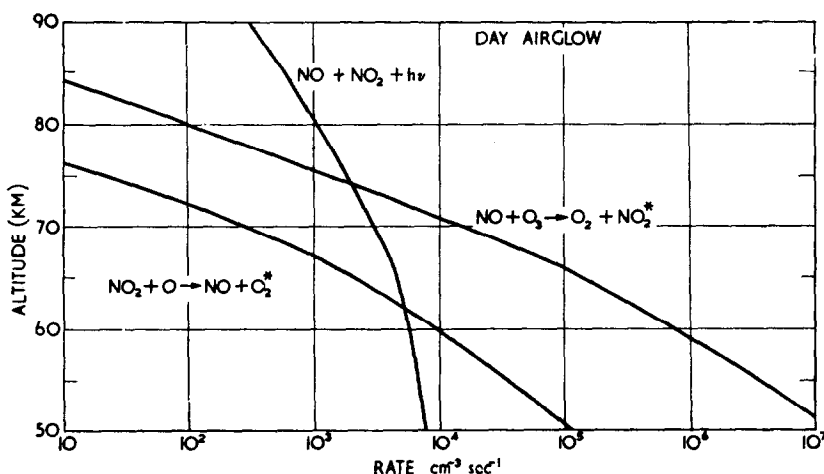

Fig. 5. Rates of the principal reactions affecting nitrogen oxides and occurring in the day airglow when nitric oxide follows the atmospheric distribution.

order of magnitude for any vertical distribution which is adopted. Owing to lack of other basic data, we adopt nitric oxide concentrations following the atmospheric distribution in order to compute the yields corresponding to processes (11), (12), and (13). The results are plotted in Fig. 5.

The continuous spectrum at $\lambda > 3900$ Å due to the reaction

$$NO + O \rightarrow NO_2 + h\nu \tag{12}$$

leads to photon emission rates per cm^3 sec not less than 10^3 photons in a layer of 30 km. Therefore, the total yield due to the continuous·day-airglow spectrum is not less than 2×10^{10} photons cm^{-2} sec^{-1}.

The reaction between nitric oxide and ozone leading to an electronic excitation of NO_2 according to

$$NO + O_3 \rightarrow O_2 + NO_2 \tag{13}$$

has a very strong rate at low altitudes. If the ozone and nitric oxide concentrations are of the same order, as adopted here, 10^7 photons cm^{-3} sec^{-1} could be emitted when there is no quenching of fluorescence by atmospheric gases.

Finally, the reaction between nitrogen peroxide and atomic oxygen which leads to an excitation of the first atmospheric system according to

$$NO_2 + O \rightarrow NO + O_2{}^* \tag{11}$$

is very effective at low heights and should play a role which may be detected in twilight spectra.

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6. CONCLUSIONS

The theoretical considerations regarding the possible effects of nitrogen oxides in the airglow have revealed that these minor constituents cannot be neglected.

Since the presence of nitric oxide in the lower ionospheric region seems to be justified in explaining its behaviour, it is conceivable that nitrogen oxides play a role in the airglow. However, in order to make such an exploration it has been necessary to assume values of the rate coefficients for various reactions in the thermosphere.

In spite of the fact that tentative values have been used because of the lack of basic laboratory data, it has been possible to draw attention to promising sources of emission, and to show how the presence of nitrogen oxides appears to offer attractive possibilities for the explanation of the airglow.

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