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Ionospheric processes and nitric oxide

by M. NICOLET

FOREWORD

The observations of the luminescent reactions appearing
in the nightglow cannot been explained by the conventional chemical
reactions. It is shown how the ionic reactions are at the origin
for the formation of nitric oxide at a height of 100 km. Ionospheric
phenomena detected by mass spectrometer are explained in that way.
"Ionospheric Processes and Nitric Oxide" will be published within
the course of the year in the Aeronomical and Planetary Sciences
section of The Journal of Geophysical Research, USA.

M. Nicolet.

AVANT-PROPOS

Les observations de réactions lumineuses apparaissant
dans la lumière du ciel nocturne ne s'expliquent pas par les
réactions chimiques habituelles. Il est démontré comment les
réactions ioniques sont à l'origine de la formation de l'oxygène
d'azote à l'altitude de 100 km. De là, les phénomènes ionosphé-
riques détectés par les spectrographes de masse sont expliqués.
"Ionospheric Processes and Nitric Oxide" sera publié au cours
de l'année dans la section : Aéronomie et sciences planétaires.
du Journal of Geophysical Research, USA.

M. Nicolet.

VOORWOORD

De waarnemingen der lichtgevende reakties, die optreden
in de nachtelijke hemel, kunnen niet uitgelegd worden aan de hand
van de gewone scheikundige reakties. Er wordt aangetoond hoe de
ionische reakties de oorsprong zijn van de vorming van stikstof-
oxyde op een hoogte van 100 km. Van daaruit worden verder de
ionosferische verschijnselen uitgelegd, die werden gedetecteerd
door massaspektrografen. "Ionospheric Processes and Nitric Oxyde"
zal in de loop van het jaar gepubliceerd worden in de afdeling :
Aëronomie en planetarische wetenschappen van de Journal of Geophysical
Research, USA.

M. Nicolet.

VORWORT

Die Beobachtungen der Lichtreaktionen, die im Nachtlicht
vorkommen, können nicht mit den gewöhnlichen chemischen Reaktionen
erklärt werden. Es wird beweist, wie die ionischen Reaktionen am
Ursprung der Formation des Stickstoffoxydes in der Höhe von 100 km
sind. So werden die ionosphärischen Phänomen, die mit Massen-
spektrografen entdeckt wurden, erklärt. "Ionospheric Processes
and Nitric Oxide" wird in der Abteilung der Aeronomie und plane-
tarischen Wissenschaften des Journal of Geophysical Research, USA,
in 1965 herausgegeben werden.

M. Nicolet.

IONOSPHERIC PROCESSES AND NITRIC OXIDE

by

Marcel NICOLET

ABSTRACT

Analysis of ionic processes in the ionosphere leads to the conclusion that nitric oxide and its ion are produced by a reaction between nitrogen molecules and molecular oxygen ions. Such a process implies a substantial increase of nitric oxide in the E layer to a value greater than the photochemical concentration. In the lower D region, N_2^+ and O_2^+ ions produced by cosmic rays are transformed into NO^+ ions. A quantitative estimate shows that these conclusions are consistent with observational data in the chemosphere and ionosphere and also suggests the explanation of the night airglow continuum.

1.- INTRODUCTION.

The theory of the origin of the D region in the terrestrial ionosphere proposed by Nicolet and Aikin [1960] indicates that it results in its lower part, from cosmic rays ionizing molecular oxygen and nitrogen and from solar Lyman-α ionizing nitric oxide during quiet solar conditions. The contribution of solar X-rays at wave-lengths less than 10 Å depends on solar activity. The minimum-to-maximum variation of intensity is a factor of several hundred in the 2-8 Å band [Friedman, 1963]. Recent observations by Aikin et al. [1964] definitely show that the role of the 2 - 10 Å band is unimportant for sufficiently quiet solar conditions. The X-ray effect occurs for the slightly disturbed sun and is predominant during flare conditions.

However, if the origin of the normal D region is well known, the problem of its structure is far from being understood due to the lack of information concerning its ionic composition. The vertical distribution of its electronic and ionic densities is only approximately known [Bourdeau, 1962; Belrose, 1964; Sagalyn and Smiddy, 1964]. Consequently, the present knowledge of the daytime and night-time D region still depends on the theoretical investigations of the physical processes involving positive and negative ions.

An excellent analysis of the present knowledge made recently by Reid [1964] shows how the role of negative ions is important. The uncertainty concerning the extent to which laboratory measurements can be applied to the formation of the D region is clearly seen in a review of the negative ion reactions by Branscomb [1964]. It appears, however, that the presence of only one ion, namely O_2^-, subject to photodetachment by visible radiation is not sufficient to explain the behaviour of the D region. The existence of NO_2^- which has an electron affinity of 92 kcal [Farragher et al., 1964], corresponding to photodetachment by ultraviolet radiation, is almost certain since it can be formed from a reaction with any atomic negative ion, or by reaction with nitric oxide as follows :

$$NO + O_2^- \rightarrow NO_2^- + O + 82 \text{ kcal.}$$
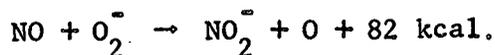
A recent discussion of the various positive and negative ionic processes by Whitten and Popoff [1964] shows how ambiguities may arise from the use of arbitrary rate coefficients to explain ionospheric data. Nevertheless, it appears difficult to avoid the conclusion that the dissociative recombination at room temperature for diatomic ions is of the order of 10^{-7} cm^{3}sec^{-1}. Thus, Biondi [1964] gives

$$\alpha_{N_2} = (2.8 \pm 0.5) \times 10^{-7} \text{ cm}^3\text{sec}^{-1} \; ; \; \alpha_{O_2} = (2.0 \pm 0.5) \times 10^{-7} \text{ cm}^3\text{sec}^{-1}.$$

Taking an average value of the dissociative recombination coefficient $\alpha_D \simeq 2 \times 10^{-7}$ cm^{3}sec^{-1} for all diatomic ions may give the correct order of magnitude of electron-ion recombination rate coefficients. Better precision cannot be claimed from an analysis of aeronomic processes without an exact knowledge of the vertical distribution of electrons and ions. As far as mutual neutralization resulting from ion-ion recombination is concerned, a value of the same order $\alpha_i = 2 \times 10^{-7}$ cm^{3}sec^{-1} for $O_2^+ + O_2^-$ and $NO^+ + NO_2^-$ may be adopted without any experimental evidence. Other values such as $\alpha_i = 10^{-8}$ cm^{3}sec^{-1} may be possible but a very precise aeronomic study of the lower D region, which is produced by cosmic rays, is needed in order to determine the effective recombination of positive ions.

The problem of charge transfer and ion-atom interchange processes remains in a state of confusion. At the present time, using laboratory measurements to obtain aeronomic estimates of rate coefficients is not a sufficiently accurate approach. Many experimental determinations do not as yet yield even order of magnitude values.

The purpose of the present paper is not, however, to review all the information available from laboratory experiments and aeronomic calculations, but to consider certain new aspects of the problem of nitric oxide production and related ionospheric studies. The analyses of recent

spectrometric observations by Barth [1964] of nitric oxide and the mass-spectrometric studies by Narcisi and Bailey [1964] involving only nitric oxide ions without molecular oxygen ions in the lower part of the D region require a different method of approach. In view of the importance of chemical reactions in the analysis of such problems, reference is made to another paper Nicolet [196-].

2.- IONIC REACTIONS AND IONIZATION EQUILIBRIUM.

The various ionic reactions have been recently considered [Nicolet and Swider, 1963] and Fig. 1 gives a general idea of the relationships between the various processes. Only the NO^+ ion disappears by dissociative recombination alone, while O_2^+ and N_2^+ are subject to ion-atom interchange reactions or to charge transfer processes, respectively. The atomic ion O^+ is transformed into molecular ions by ion-atom interchange reactions. The essential exothermic processes which are considered here are as follows :

$$(\gamma_1) \; ; \; O^+(^4S) + N_2(^1\Sigma) \; \rightarrow \; NO^+(^1\Sigma) + N(^4S) + 25 \text{ kcal} \tag{1}$$

$$(\gamma_2) \; ; \; O^+(^4S) + O_2(^3\Sigma) \; \rightarrow \; O_2^+(^2\Pi) + O(^3P) + 35 \text{ kcal} \tag{2}$$

$$(\gamma_3) \; ; \; O^+(^4S) + NO(^2\Pi) \; \rightarrow \; NO^+(^1\Sigma) + O(^3P) + 100 \text{ kcal} \tag{1a}$$

$$(\gamma_4) \; ; \; O^+(^4S) + NO(^2\Pi) \; \rightarrow \; O_2^+(^2\Pi) + N(^4S) + 4 \text{ kcal} \tag{2a}$$

$$(\gamma_5) \; ; \; O_2^+(^2\Pi) + NO(^2\Pi) \; \rightarrow \; NO^+(^1\Sigma) + O_2(^3\Sigma) + 45 \text{ kcal} \tag{3}$$

$$(\gamma_6) \; ; \; O_2^+(^2\Pi) + N(^4S) \; \rightarrow \; NO^+(^1\Sigma) + O(^3P) + 91 \text{ kcal} \tag{4}$$

$$(\gamma_7) \; ; \; O_2^+(^2\Pi) + N_2(^1\Sigma) \; \rightarrow \; NO^+(^1\Sigma) + NO(^2\Pi) + 16 \text{ kcal} \tag{5}$$

$$(\gamma_8) \; ; \; N_2^+(^2\Sigma) + O(^3P) \; \rightarrow \; O^+(^4S) + N_2(^1\Sigma) + 45 \text{ kcal} \tag{6a}$$

$$(\gamma_9) \; ; \; N_2^+(^2\Sigma) + O_2(^3\Sigma) \; \rightarrow \; O_2^+(^2\Pi) + N_2(^1\Sigma) + 81 \text{ kcal} \tag{6b}$$
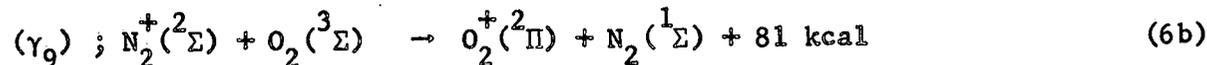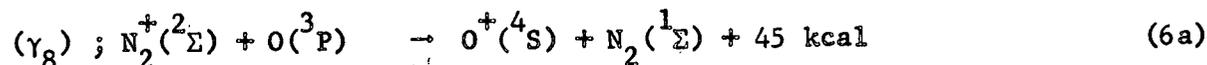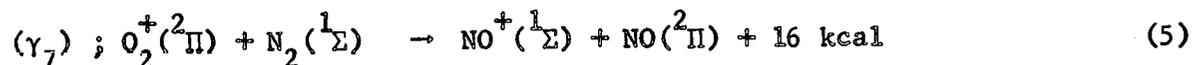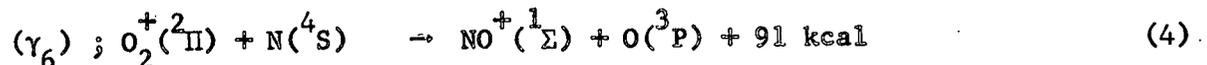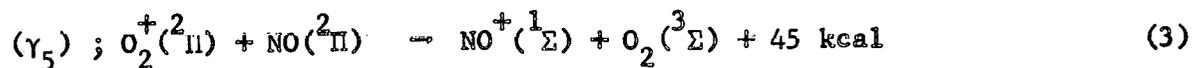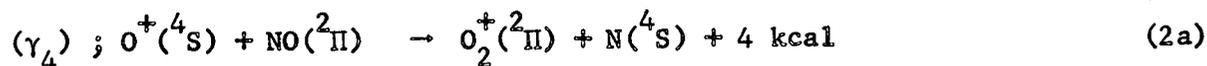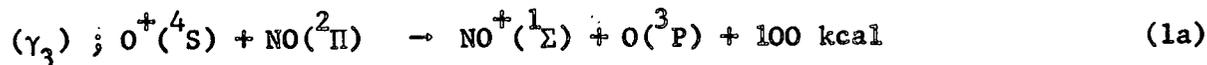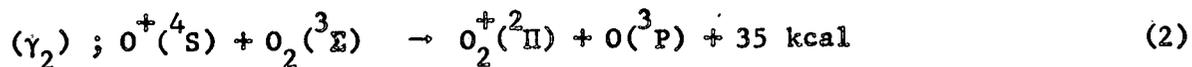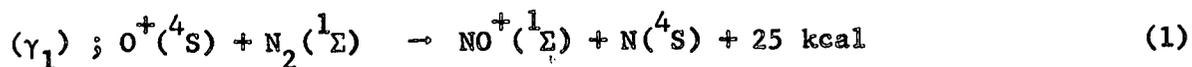
NITRIC OXIDE REACTIONS

CHEMOSPHERE

$$NO + h\nu - J_{NO} \rightarrow N + O$$

$$N + O(+M) - b_1 \rightarrow NO\ (+M) + h\nu$$

$$N + O_2 - b_7 \rightarrow O + NO$$

$$N + NO - b_6 \rightarrow O + N_2$$

IONOSPHERE

$$NO + h\nu - I_{NO} \rightarrow e + NO^+ - \alpha_{NO} \rightarrow N + O$$

$\gamma_5 \quad \gamma_6 \quad \gamma_7$

$$NO^+ \quad N^+ \quad N_2^+$$

$$O_2 + h\nu - I_{O_2} \rightarrow e + O_2^+ - \alpha_{O_2} \rightarrow O + O$$

$\gamma_9 \quad \gamma_2 \quad \gamma_4$

$$O_2^+ \quad NO^+$$

$$+ NO - \gamma_3 \rightarrow O + NO^+\ (^1\Sigma)$$

$$O + h\nu - I_O \rightarrow e + O^+$$

$$(O_2 \rightarrow O + O^+) \quad + N_2 - \gamma_1 \rightarrow N + NO^+\ (^1\Sigma)$$

$\gamma_{14} \quad \gamma_8$

$$O_2^+ \quad O^+$$

$$\alpha_{N_2} \rightarrow N + N$$

$$N_2 + h\nu - I_{N_2} \rightarrow e + N_2^+ - + O - \gamma_{15}^{**} \rightarrow N + NO^+\ (^3\Pi)$$

$$+ O_2 - \gamma_{15}^{*} \rightarrow NO + NO^+\ (^3\Pi)$$

$$+ N \quad + NO - \gamma_{16} \rightarrow N_2 + NO^+\ (^1\Sigma)$$

γ_{11}

$$O \quad NO \quad + O_2 - \gamma_{12} \rightarrow O + NO^+\ (^3\Pi)$$

$$+ \quad \gamma_{10} \quad +$$

$$N + h\nu - I_N \rightarrow e + N^+$$

$$(N_2 \rightarrow N + N^+) \quad + NO - \gamma_{13} \rightarrow N + NO^+\ (^1\Sigma, ^3\Pi)$$
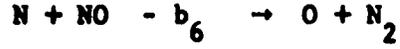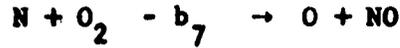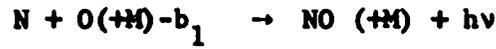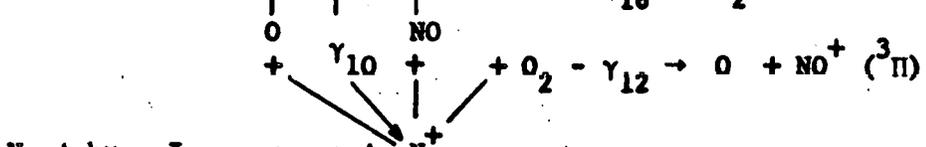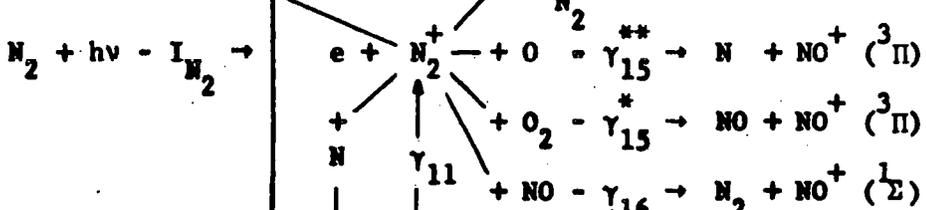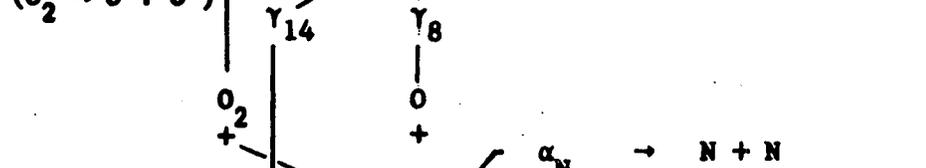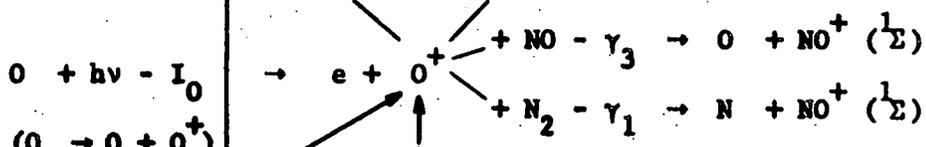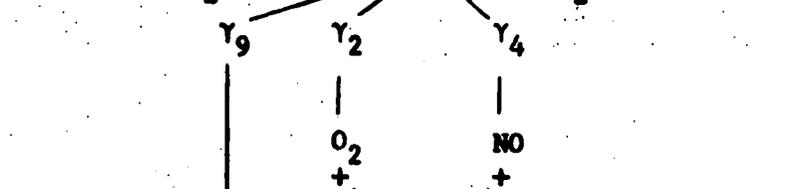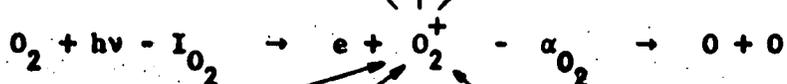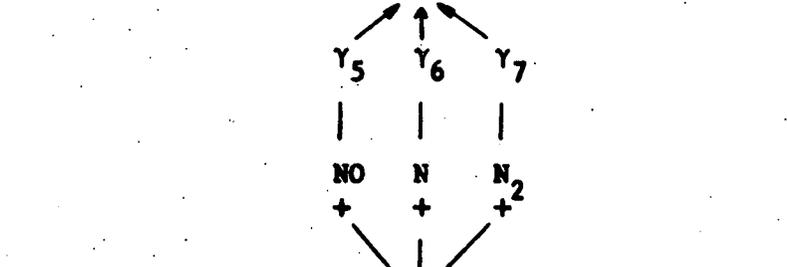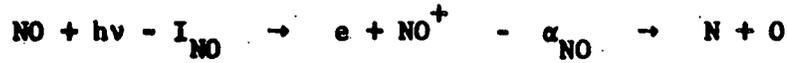
Fig. 1.-

Reactions (1) and (5) producing $NO^+(v'' \leq 3)$ and $NO^+(v'' \leq 2)$, respectively, may correspond to luminescent reactions : $\Delta v = 1$ near 4.3μ, $\Delta v = 2$ near 2.15μ and $\Delta v = 3$ near 1.5μ.

The loss processes (1) and (2) of O^+ are the only ones to be considered, and their rate coefficients γ_1 and γ_2 are about $10^{-12 \pm 1} cm^3 sec^{-1}$. Reaction (5) is a loss process of O_2^+ with a low rate coefficient for which we adopt $\gamma_7 = 10^{-16 \pm 1} cm^3 sec^1$. The loss rate of O_2^+ by such a process is certainly negligible in the F layers, but cannot be neglected in the lower ionosphere [Nicolet and Swider, 1963]. It may compete with the dissociative recombination.

$$(\alpha_{O_2}) \; ; \; O_2^+ + e \rightarrow O^0 + O'' \qquad (7)$$
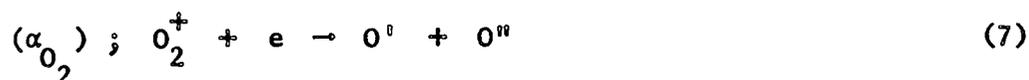
which leads to oxygen atoms in ^3P, ^1D and ^1S states.

As far as the charge transfers (6) are concerned, they are rapid enough to be the essential loss processes of N_2^+ in the D and E regions. The dissociative recombination process

$$(\alpha_{N_2}) \; ; \; N_2^+ + e \rightarrow N^0 + N'', \qquad (8)$$

which may lead to nitrogen atoms in ^4S, ^2D and ^2P states, is relatively important only in the F region.

The dissociative recombination of NO^+

$$(\alpha_{NO}) \; ; \; NO^+ + e \rightarrow N^0 + O^0 \qquad (9)$$
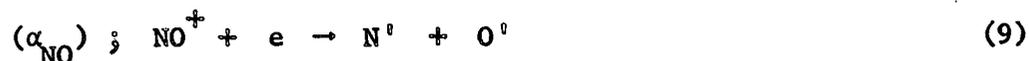
is the only loss process of this ion. It may give nitrogen atoms in ^4S and ^2D states and oxygen atoms in ^3P and ^1D states.

An order of magnitude, at sufficiently low temperatures, for the dissociative recombination coefficient such as

$$\alpha_D = \alpha_{N_2} \simeq \alpha_{O_2} \simeq \alpha_{NO} \simeq 2 \times 10^{-7} \, cm^3 sec^{-1} \qquad (10)$$

is only a sufficient approximation for illustrative purposes. A precise aeronomic study requires a precision better than 20 percent.

The negative ions of first importance are the molecular ions O_2^- and NO_2^- which must occur in the lower D region. A (not precise) value for the recombination coefficient with positive ions can be obtained by taking it equal to the dissociative recombination coefficient.

$$\alpha_i = \alpha_D \simeq 2 \times 10^{-7} \, cm^3 \, sec^{-1} \tag{11a}$$

but not smaller than

$$\alpha_i \geq 10^{-8} \, cm^3 \, sec^{-1} \tag{11b}$$

If I_{N_2}, I_{O_2}, I_O and I_{NO} are the photo-ionization rate coefficient of N_2, O_2, O and NO, respectively, it is possible to write the general ionization equations for equilibrium conditions. If λ is the ratio of negative ions to electrons, these relations are

$$n^+(N_2) = \frac{n(N_2) \, I_{N_2}}{\gamma_8 n(O) + \gamma_9 n(O_2) + (\alpha_{N_2} + \lambda\alpha_i)n_e} \tag{12}$$

$$n^+(O) = \frac{n(O)[I_O + \gamma_8 \, n^+(N_2)]}{\gamma_1 n(N_2) + \gamma_2 n(O_2) + (\gamma_3 + \gamma_4)n(NO)} \tag{13}$$

$$n^+(O_2) = \frac{n(O_2)[I_{O_2} + \gamma_2 n^+(O) + \gamma_9 n^+(N_2)] + \gamma_4 n^+(O) \, n(NO)}{\gamma_5 n(NO) + \gamma_6 n(N) + \gamma_7 n(N_2) + (\alpha_{O_2} + \lambda\alpha_i)n_e} \tag{14}$$

$$n^+(NO) = \frac{n(NO)[I_{NO}+\gamma_3 n^+(O) + \gamma_5 n^+(O_2)] + \gamma_1 n(N_2)n^+(O) + [\gamma_6 n(N) + \gamma_7 n(N_2)n^+(O_2)}{(\alpha_{NO} + \lambda\alpha_i)n_e} \quad (15)$$

3.- NITRIC OXIDE AND ATOMIC NITROGEN.

As pointed out earlier, the ionic processes can play a role in the production of nitrogen atoms and of nitric oxide. There is a production of nitrogen atoms,

$$\frac{dn(N)}{dt} = \alpha_{NO} n^+(NO)n_e + \gamma_1 n^+(O) n(N_2) + 2\alpha_{N_2} n^+(N_2)n_e \quad . \quad (16)$$

A production of nitric oxide comes from

$$\frac{dn(NO)}{dt} = \gamma_7 n(N_2) n^+(O_2) \quad (17)$$

These productions of N and NO by ionic reactions must be added to chemical production [Nicolet, 196-] by

$$\frac{dn(N)}{dt} = n(NO)J_{NO} + 2n(N_2) J_{N_2} \quad (18)$$

corresponding to the photodissociation of NO and N_2, and

$$\frac{dn(NO)}{dt} = [b_1 n(O) + b_7 n(O_2)]n(N) \quad (19)$$

corresponding to the reactions

$$(b_1) \; ; \; N + O(+ M) \; \rightarrow \; NO(+ M) + 150 \; kcal \quad (20)$$

$$(b_7) \; ; \; N + O_2 \quad \rightarrow \; NO + O + 32 \; kcal \; . \quad (21)$$
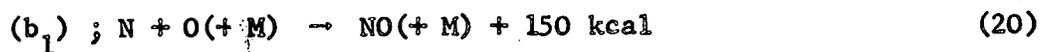
The common loss process

$$(b_6) \; ; \quad N + NO \rightarrow N_2 + O + 75 \text{ kcal} \tag{22}$$

combines with (20) and (21) as

$$- \frac{dn(N)}{dt} = [b_1 \, n(O) + b_6 \, n(NO) + b_7 \, n(O_2)] \, n(N) \tag{23}$$

and

$$- \frac{dn(NO)}{dt} = n(NO) \, J_{NO} + b_6 \, n(N) \, n(NO) \tag{24}$$

Using the ionization equilibrium equations (12) to (15) which can be applied to the D, E and F_1 layers, plus the chemical reactions, the following expressions are obtained for NO and N, neglecting the term $\lambda \alpha_i \, n^+(NO) n_e$

$$\frac{dn(NO)}{dt} + n(NO) \, [J_{NO} + I_{NO} + b_6 \, n(N) + (\gamma_3 + \gamma_4) n^+(O) + \gamma_5 \, n^+(O_2)] =$$

$$n(N) \, [b_1 \, n(O) + b_7 \, n(O_2)] + \gamma_7 \, n^+(O_2) \, n(N_2) \, . \tag{25}$$

$$\frac{dn(N)}{dt} + n(N) \, [b_1 \, n(O) + b_6 \, n(NO) + b_7 \, n(O_2)] = n(NO) \, [J_{NO} + I_{NO} + (\gamma_3 + \gamma_4) n^+(O)$$

$$+ \gamma_5 n^+(O_2)] + n(N_2) \, [2J_{N_2} + 2\gamma_1 \, n^+(O) + \gamma_7 \, n^+(O_2)] + 2 \, \alpha_{N_2} \, n^+(N_2) n_e \tag{26}$$

The conditions for the simultaneous variation of n(NO) and n(N) can be conveniently written, from (25) and (26),

$$\frac{dn(NO)}{dt} + \frac{dn(N)}{dt} + 2b_6 \, n(NO) \, n(N) =$$

$$2n(N_2) \left[J_{N_2} + \gamma_7 \, n^+(O_2) + \gamma_1 \, n^+(O) \right] + 2\alpha_{N_2} \, n^+(N_2)n_e \qquad (27)$$

For equilibrium conditions, (27) leads to

$$b_6 n(NO) \, n(N) = n(N_2) \left[J_{N_2} + \gamma_7 \, n^+(O_2) + \gamma_1 \, n^+(O) \right] + \alpha_{N_2} \, n^+(N_2)n_e \qquad (28)$$

or

$$n(N) \left[b_1 \, n(O) + b_7 \, n(O_2) \right] = n(N_2) \left[J_{N_2} + \gamma_1 \, n^+(O) \right] +$$

$$+ n(NO) \left[J_{NO} + I_{NO} + (\gamma_3 + \gamma_4) \, n^+(O) + \gamma_5 \, n^+(O_2) \right] \qquad (29)$$

The effect of ionic reactions on N and NO concentrations is easily understood since the terms with the symbol gamma correspond to the ionospheric production of atomic nitrogen or nitric oxide.

4.- IONOSPHERIC CONDITIONS IN VARIOUS IONOSPHERIC LAYERS.

Equations (12) to (15) lead to the general ionization for steady state conditions

$$n(N_2) \, I_{N_2} + n(O) \, I_O + n(O_2)I_{O_2} + n(NO) \, I_{NO} =$$

$$n_e \left\{ n^+(N_2) \left[\alpha_{N_2} + \lambda\alpha_i \right] + n^+(O_2) \left[\alpha_{O_2} + \lambda\alpha_i \right] + n^+(NO) \left[\alpha_{NO} + \lambda\alpha_i \right] \right\} \quad (30)$$

All loss processes of electrons occur by molecular recombination through ionic reactions.

The essential characteristics of the loss processes for N_2^+ ions is the competition between charge transfer and dissociative recombination.

The absence of N_2^+ ions in the E layer is due to the effect of charge transfer. Assuming that the N_2^+ loss in the D region by dissociative recombination is inappreciable compared with other processes, (12) becomes

$$n^+(N_2) \ [\gamma_8 \ n(O_2) + \gamma_9 \ n(O)] = X \ n(N_2) \ I_{N_2} \qquad (31)$$

where $X = 1$. The parameter $0 \le X \le 1$ reaches its minimum value in the F_2 layer; it can be taken as unity in the D and E layers and is still about 1 in the F_1 layer. This leads to a simplification of (30) for the lower ionospheric layers where we are considering the behaviour of production of NO and NO^+. (30) can be conveniently written as follows :

$$X.n(N_2) \ I_{N_2} + n(O) \ I_O + n(O_2) \ I_{O_2} + n(NO) \ I_{NO} =$$

$$n_e \left\{ n^+(O_2) \ [\alpha_{O_2} + \lambda\alpha_i] + n^+(NO) \ [\alpha_{NO} + \lambda\alpha_i] \right\} \qquad (32)$$

where $X = 1$.

It is natural to compare (32) with the ionization equation (15) related to NO^+ :

$$n_e \ n^+(NO) \ [\alpha_{NO} + \lambda\alpha_i] = n^+(O_2) \ [\gamma_6 n(N) + \gamma_7 n(N_2)] + n^+(O) \ \gamma_1 \ n(N_2)$$

$$n(NO) \ [I_{NO} + \gamma_3 \ n^+(O) + \gamma_5 \ n^+(O_2)] \qquad (33)$$

At sufficiently high altitudes the first term on the right of (33) certainly becomes negligible and the presence of NO^+ ions depends on the direct photoionization and especially on the reactions involving the atomic oxygen ion. An attempt at determining the concentration of NO^+ in the F region must be made on the basis of such an interpretation. In the E layer, where atomic oxygen ions do not play an important role and where the NO^+ concentration is comparable to that of O_2^+, the reaction between O_2^+ and N_2

cannot be considered as a negligible process. The direct photoionization of NO by Lyman-α is certainly the essential NO ionization process in the D region, particularly during quiet solar conditions when the X-ray ionization is inappreciable. However, the penetration of Lyman-α into the lower D region is limited by molecular oxygen, and the ionization produced there is due to cosmic rays. Under such conditions, (33) becomes

$$n_e n^+(NO) \left[\alpha_{NO} + \lambda \alpha_i \right] = n^+(O_2) \left[\gamma_5 \, n(NO) + \gamma_6 \, n(N) + \gamma_7 \, n(N_2) \right] \qquad (34)$$

and since atomic nitrogen does not exist in sufficient quantity,

$$\frac{n_e n^+(NO)}{n^+(O_2)} = \frac{\gamma_7 \, n(N_2) + \gamma_5 \, n(NO)}{\alpha_{NO} + \lambda \alpha_i} \qquad (35)$$

where is the proper ionization equation to apply below the region where Lyman-α ionizes NO.

Taking $\alpha_{NO} + \lambda \alpha_i \simeq \alpha_{O_2} + \lambda \alpha_i$ in the general equation (32) and representing the production processes by q, we write :

$$q = (1 + \lambda) \, (\alpha_D + \lambda \alpha_i) n_e^2 . \qquad (36)$$

Introducing (36) in (35), the following ratio is obtained

$$\frac{n^+(NO)}{n^+(O_2)} = \frac{\gamma_7 \, n(N_2) + \gamma_5 \, n(NO)}{\left[(\alpha_D + \lambda \alpha_i) q / (1 + \lambda) \right]^{1/2}} , \qquad (37)$$

if NO^+ is the principal ion.

At 60 km, where only ionization by cosmic rays occurs during the normal day-time and night-time conditions, $n^+(NO) \gg n^+(O_2)$, and (36) is equivalent to

$$q = (\alpha_D + \lambda \alpha_i) \, n^+(NO) n_e = \left[\alpha_i + \alpha_D / \lambda \right] \left[n^+(NO) \right]^2 \qquad (38)$$

With a cosmic ray production of not less than 5×10^{-2} ions $cm^{-3} sec^{-1}$, the time to reach equilibrium conditions is always less than one hour.

Exact ionospheric conditions cannot presently be determined since the rate coefficient γ_7 is not known. A value $\gamma_7 = 10^{-16 \pm 1}$ may be adopted if O_2^+ has to be eliminated in the lower D region. This process has not been observed in the laboratory due to its low absolute value and it is difficult to determine how it varies with temperature. Nevertheless, it seems that it is the process which can make the observational results of Narcisi and Bailey [1964] understandable. The absence of O_2^+ at 65 km with a ratio $n(NO^+)/n^+(O_2)$ greater than 50 below 75 km and a rapid decrease to less than 5 near the mesopause require processes other than that due to dissociative recombination. It is difficult to see how the X ray production, as compared with the Lyman-α intensity, could favour such a vertical ionic distribution.

In the E layer, it could be claimed, however, that the process between O_2^+ and N_2 is negligible and, hence, that it is not responsible for the presence of NO^+. Nevertheless, such a conclusion is premature. Thus, finding in observational data [Holmes et al., 1964] that $n^+(NO) \simeq n^+(O_2)$ in the day-time E layer, equation (33) at 100 km leads to

$$n_e n^+(NO) \alpha_{NO} = 10^5 \times 5 \times 10^4 \times 2 \times 10^{-7} = 1000 \ cm^{-3} sec^{-1}. \quad (39)$$

As a result, we are led to consider that a process like $O^+ + N_2 \rightarrow NO^+ + N$ or $n(NO) I_{NO}$ is, in fact, important. If $n(NO)$ is $10^8 \ cm^{-3}$ or less, the direct photoionization is then less than $50 \ cm^{-3} sec^{-1}$. The best attempt at determining a production of more than 100 NO^+ ions $cm^{-3} sec^{-1}$ at 100 km would be to consider a very small concentration of O^+ ions. The X-ray production would always be the essential process.

To obtain information on the existence of the reaction process $O_2^+ + N_2 \rightarrow NO^+ + NO$, it is perhaps necessary to consider night-time conditions in the E layer. In view of the observational results obtained for the night-time E layer [Holmes et al., 1964], we may put forward the

hypothesis that the ratio $n^+(NO) > n^+(O_2)$ depends on the ion-interchange process, i.e.

$$\gamma_5 \ n(NO) + \gamma_7 \ n(N_2) + \gamma_{O_2} \ n_e \leq 10^{-3} \ sec^{-1} \tag{40}$$

With $n(N_2) \simeq 10^{13}$ to $10^{12} \ cm^{-3}$ and $\gamma_7 \simeq 10^{-16}$ to $10^{-15} \ cm^3 sec^{-1}$, consideration must be given to the process involving O_2^+ and N_2. However, it is scarcely worth pursuing this a present time since rocket and laboratory experiments are not yet sufficiently developed. The uncertainties are necessarily very great since the rate coefficients are not as yet determined and since the observational results are inadequate. It would be unwise to abandon either of the processes under discussion $\gamma_1 n^+(O)$ or $(\gamma_5 + \gamma_7) \ n^+(O_2)$ because of lack of accord with one or another particular result.

It is worth pointing out that, if the dominant process during daytime conditions for NO^+ ions is ion-atom interchange with atomic oxygen ions, the problem of explaining the whole situation becomes almost impossible. For example, assuming $\alpha_{NO} \simeq \alpha_{O_2} = 2 \times 10^{-7} cm^3 sec^{-1}$ and 10^5 electrons cm^{-3} at 100 km, equation (32) leads to

$$\alpha n_e^2 = q = 2000 \ electrons \ cm^{-3} sec^{-1} \tag{41}$$

which is an acceptable value for the electronic production at this height level. On the other hand, (33) can be conveniently written as follows

$$\alpha n^+(O_2)n_e = q - \gamma_1 \ n(N_2) \ n^+(O) \tag{42a}$$

and

$$\alpha n^+(NO)n_e = \gamma_1 \ n^+(N_2) \ n^+(O) \ . \tag{42b}$$

In order to attain a ratio $n^+(NO)/n^+(O_2) \simeq 1$, it would be necessary to assume that the electron production by atomic oxygen is at least 50 percent

of the total production at 100 km. Such a requirement cannot be accepted since the photoionization of O_2 and N_2 cannot be less important than that of atomic oxygen at 100 km and below. Obviously the recombination coefficient of NO^+ should be less than that of O_2^+ to relate the production of nitric oxide ions only to the presence of atomic oxygen ions.

The charge transfer $O + N_2^+$ cannot play an important role in the production of atomic oxygen ions at relatively low altitudes ; the N_2^+ concentration is too low in the lower E layer to be sufficient to produce the ionic density which is needed.

At present, it appears that the ion-atom interchange of O_2^+ cannot be excluded and the following equation can be written in the E layer and D region where negative ions are not important,

$$\alpha_{NO} n^+(NO) n_e = n^+(O_2)[\gamma_5 n(NO) + \gamma_7 n(N_2)] + n(NO) I_{NO}. \qquad (43)$$

5.- TOTAL PRODUCTION OF NITRIC OXIDE.

An attempt to determine the absolute concentrations of nitric oxide and atomic nitrogen in the D and E regions is difficult since the ionospheric rate coefficients are not known. However, starting from (28) and (29), the NO concentration is given by a quadratic equation which may be conveniently written as follows

$$n(NO) = \frac{b_1 n(O) + b_7 n(O_2)}{b_6} \, ,$$

$$\frac{n(N_2) [J_{N_2} + \gamma_1 n^+(O) + \gamma_7 n^+(O_2)]}{n(N_2)[J_{N_2} + \gamma_1 n^+(O)] + n(NO)[J_{NO} + I_{NO} + (\gamma_3 + \gamma_4)n^+(O) + \gamma_5 n^+(O_2)]}$$

$$(44)$$

If we consider that the production of nitrogen atoms from N_2 is important, we obtain

$$n(NO) = \frac{b_1 n(O) + b_7 n(O_2)}{b_6} \left[1 + \frac{\gamma_7 n^+(O_2)}{J_2 + \gamma_1 n^+(O)} \right]. \tag{45}$$

The limit, with $\gamma_1 n^+(O) > \gamma_7 n^+(O_2)$ corresponding to the F region, is

$$n^*(NO) = \frac{b_1 n(O) + b_7 n(O_2)}{b_6} \tag{46}$$

since the ion-atom interchange process in which O^+ is involved increases rapidly with altitudes. $n^*(NO)$ corresponds to the photochemical equilibrium value given by [Nicolet, 196-]

$$\frac{n(NO)}{n(N)} = \frac{b_1 n(O) + b_7 n(O_2)}{b_6 n(N) + J_{NO} + I_{NO}} \tag{47}$$

with the following requirement

$$n(N) > \frac{N_{NO} + I_{NO}}{b_6} \approx 2.5 \times 10^4 \, cm^3 \, sec^{-1}. \tag{48}$$

For example, such conditions can be applied at 150 km in the F_1 layer where

$$n(N) = \frac{n(N_2) \left[\gamma_1 n^+(O) + I_{N_2} (1-X) \right]}{b_6 \, n^*(NO)} \tag{49}$$

which shows that the production of nitrogen atoms is essentially due to the ion-atom interchange process.

At sufficiently low altitudes, the production of nitrogen atoms

from nitric oxide is important. Thus (44) is written

$$n^2(NO) = n^*(NO) \frac{n(N_2)\left[J_{N2} + \gamma_1 n^+(0) + \gamma_7 n^+(0_2)\right]}{J_{NO} + I_{NO} + \left[\gamma_3 + \gamma_4\right] n^+(0) + \gamma_5 n^+(0_2)} \qquad (50a)$$

and

$$n^2(NO) \simeq n^*(NO) \frac{n(N_2)\left[J_{N_2} + \gamma_1 n^+(0) + \gamma_7 n^+(0_2)\right]}{J_{NO} + I_{NO}} \qquad (50b)$$

which leads to

$$\frac{n(NO)}{n(N)} = \frac{n^*(NO) \, b_6}{I_{NO} + J_{NO}} = 5 \times 10^{-5} \, n^*(NO). \qquad (51)$$

Thus, the atomic nitrogen concentration would be, for such conditions, less than that of nitric oxide where $n^*(NO) > 2 \times 10^4 cm^{-3}$. This inequality is, in fact, satisfied everywhere as shown in Fig. 2. If we consider again the conditions at 100 km where

$$n^*(NO) \simeq 10^6 cm^{-3}, \; n(N_2) \simeq 10^{13} cm^{-3}, \; J_{NO} + I_{NO} \simeq 5 \times 10^{-7} sec^{-1},$$

equation (50b) leads to

$$n(NO) = 5 \times 10^{12} \left[J_{N_2} + \gamma_1 n^+(0) + \gamma_7 n^+(0_2)\right]^{\frac{1}{2}} cm^{-3}. \qquad (52)$$

Any value of a rate coefficient in the bracket of (52) not less than $4 \times 10^{-14} sec^{-1}$ leads to $n(NO) > n^*(NO) = 10^6 \, cm^3 sec^{-1}$; that is a value greater than the photochemical value. If the rate coefficient $\gamma_7 n^+(0_2)$ reaches values between 10^{-11} and $10^{-10} \, sec^{-1}$, the nitric oxide
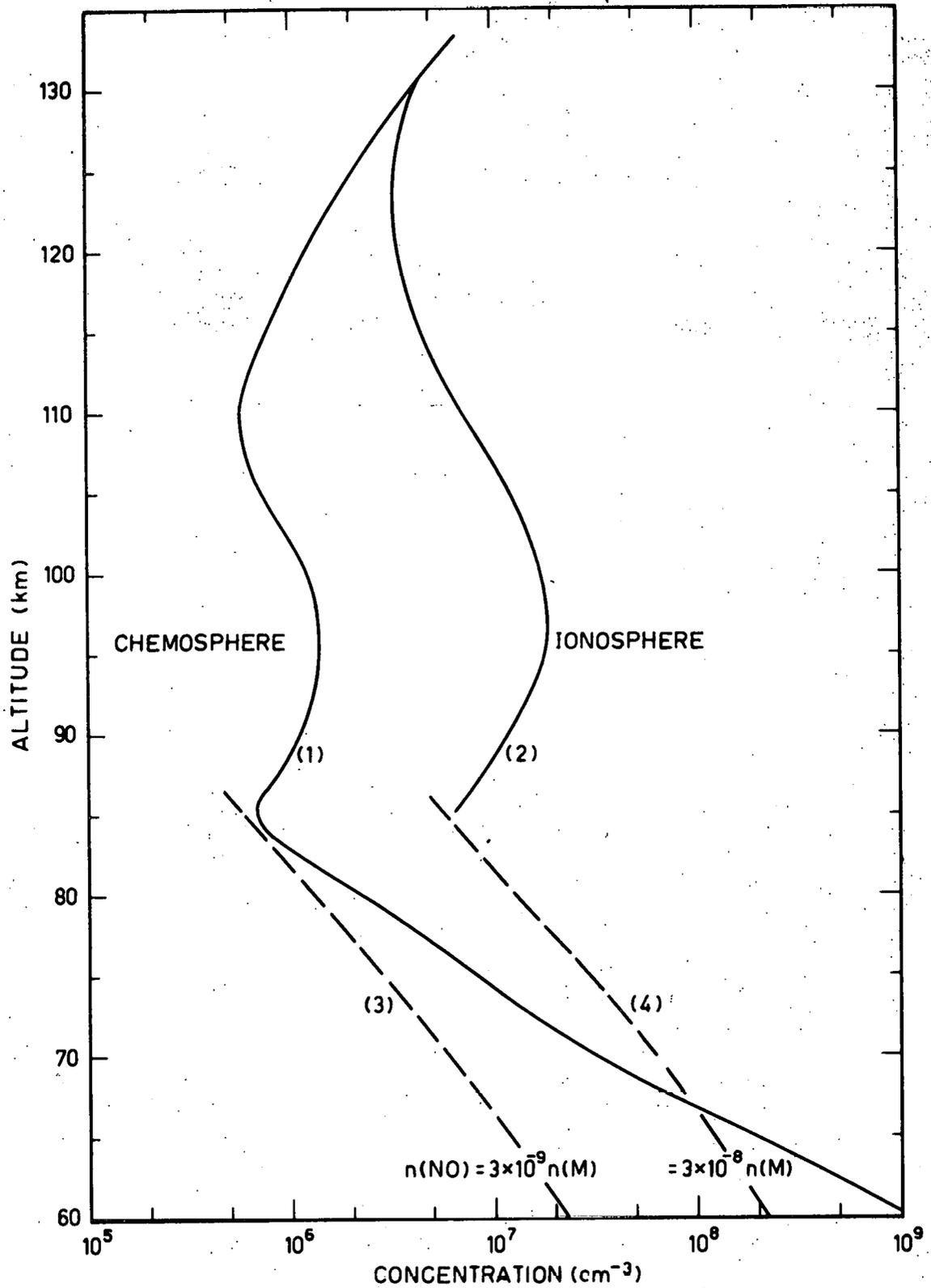
Fig. 2.- Vertical distribution of nitric oxide. (1) Photoequilibrium
conditions in the chemosphere; (2) photoequilibrium conditions
in the ionosphere; (3) and (4) mixing conditions.

concentration is between 2×10^7 and 5×10^7 $cm^3 sec^{-1}$.

An attempt may be made to determine the vertical distribution of NO for photoionization equilibrium conditions. Due to the lack of inform- ation concerning the ratio $n^+(NO)/n^+(O_2)$ between 85 km and 110 km, we assume that the electronic concentration increases from 2.5×10^3 cm^{-3} at 85 km to 10^4 cm^{-3} at 90 km and 1×10^5 at 100 km with a rate coefficient 10^{-16} $n_e sec^{-1}$ instead of $\gamma_7 n^+(O_2) sec^{-1}$. With such a hypothesis an appro- ximate form of the vertical distribution can be obtained. Fig. 2 illustrates the effect of the production of NO by the reaction between O_2^+ and NO..The two curves above 85 km show the vertical distribution of nitric oxide, as a function of chemical reactions and ion-atom interchange process during daytime conditions.

The average value of n(NO) is about 10^7 cm^{-3} and, with a thickness of about 30 km, the total content is not less than 5×10^{13} molecules cm^{-2}. Since Barth [1964] gives 1.7×10^{14} cm^{-2} above 85 km, it is best at present to regard the proposed solution as the possible mechanism. However, no definite statements are possible in such aeronomic problems without prior knowledge of the appropriate coefficients.

As was mentioned above, the mesospheric problem of nitric oxide indicates that the density distribution depends on equilibrium conditions near the mesopause. Variations will occur depending on X-ray effects; particularly during high solar activity conditions. No attempt will be made here to illustrate this since we would then be forced into adopting all rate coefficients based on laboratory measurements as being applicable or of choosing aeronomic parameters which are as yet unknown. The curves with n(NO) = 3×10^{-9} n(M) and 3×10^{-8} n(M) shown in Fig. 2, indicate that a very large change may occur in the upper mesosphere. The change from chemical equilibrium conditions to mixing conditions is very marked. Obviously the actual situation is verycomplicated since the life-time of NO is not short between 65 and 85 km. In treating nonequilibrium cases we have to consider different ionization conditions (intensity and duration) in order to relate the equilibrium concentrations to the rate

of production of NO, NO$^+$ and O$_2^+$. In any case, the use of recent laboratory measurements for nitric oxide reactions results in values of NO between 10 and 100 times the value adopted by Nicolet and Aikin in the mesosphere.

The essential conclusion is that there is a possibility of explaining by one ionic process the predominance of NO$^+$ ions in the lower D region and an excess of NO in the region of 100 km. It seems that Barth's observations should be interpreted by considering a peak in the vertical distribution of NO. Normalizing to his value of 1.7×10^{14} molecules cm^{-2} for the column density of nitric oxide above 85 km, the values of n(NO) in Fig. 2 should be multiplied by a factor of only 3 to give the same total content.

6.- NITRIC OXIDE AND THE AIRGLOW CONTINUUM.

Several authors have suggested that

$$O + NO \rightarrow NO_2 + h\nu \ (\lambda > 3750 \ \overset{o}{A}) \tag{53}$$
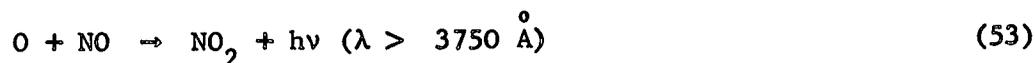
contributes to the airglow continuum [Krassovsky, 1951; Bates, 1954; Nicolet, 1955; Doherty and Jonathan, 1964]. It may correspond to the continuum emission with a peak around 100 km observed by rocket [Packer, 1961]. Adopting the absolute value of 6.4×10^{-17} cm^3 sec^{-1} obtained by Fontijn et al. [1964] with the following division : 3.2×10^{-17} cm^3 sec^{-1} for $\lambda < 7250$ A and $\lambda > 7250$ A, [Nicolet, 196-], it is possible to make a comparison with the observed value of the airglow continuum. An approximate value of about 6×10^9 photons cm^{-2} sec^{-1} is given [Krassovsky et al., 1962] for the spectral range $\lambda\lambda$ 4000 - 7000 A.

With the NO vertical distribution shown in Fig. 2 and approximate concentrations of atomic oxygen for night-time conditions, it is possible to determine the general emission of the continuum. The result is illustrated in Fig. 3 which gives the number of photons cm^{-3} sec^{-1} between 75 km and 115 km. The total emission corresponds to 3.4×10^9 photons cm^{-2} sec^{-1} or 1.7×10^9 photons cm^{-2} sec^{-1} for the 4000 - 7250 A range. Normalizing to the observed value, the theoretical flux should be multiplied
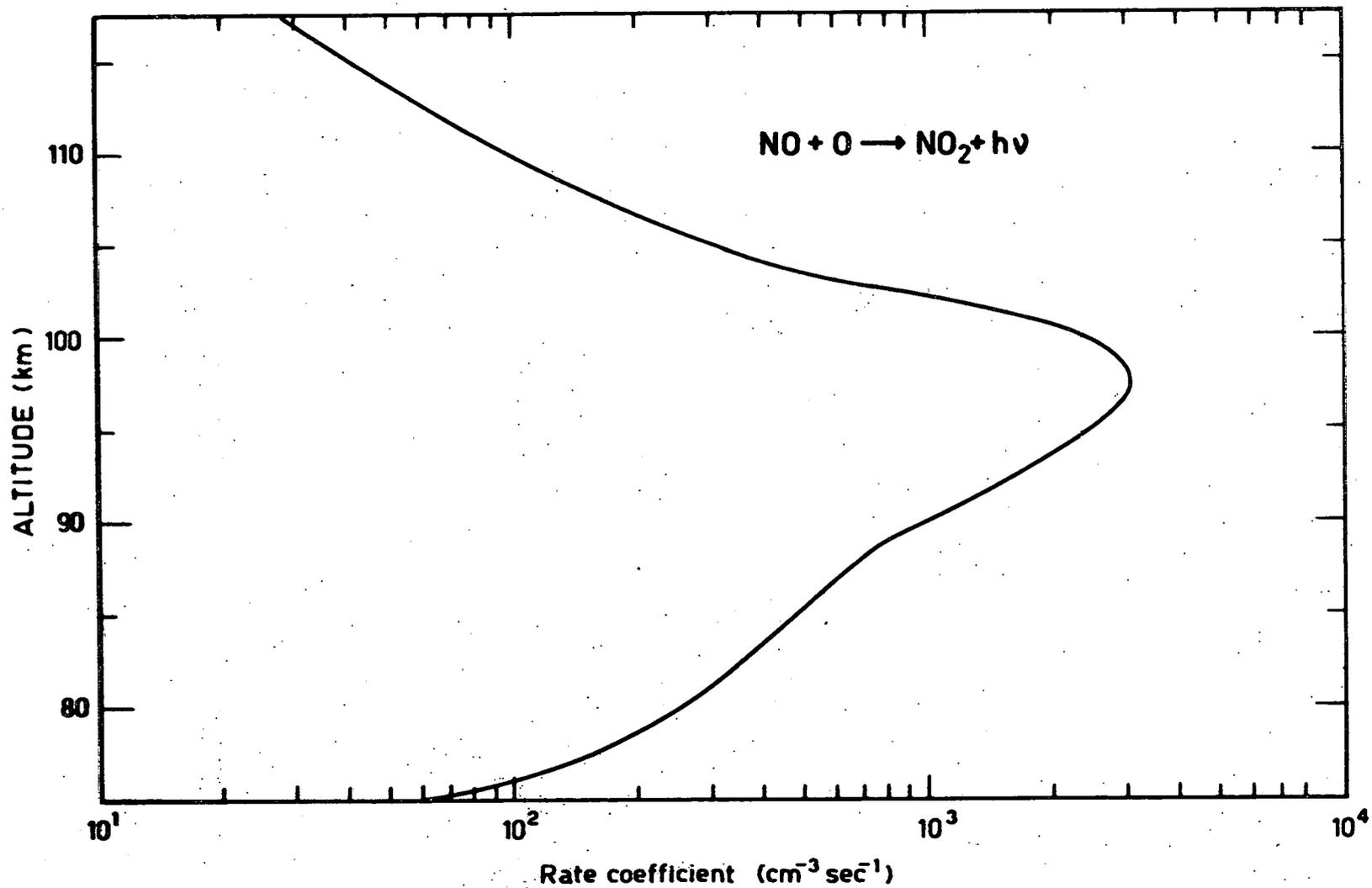
Fig. 3.- Number of photons $\lambda > 4000$ Å cm^{-3} sec^{-1}

by a factor of about 3 to give the same number of photons $cm^{-2} sec^{-1}$. This is the same factor which was used to obtain the total number of NO molecules observed by Barth [1964]. This may be pure coincidence. Nevertheless it corresponds to an average value of 3×10^{-16} $cm^3 sec^{-1}$ for the rate coefficient of the reaction $O_2^+ + N_2 \rightarrow NO + NO^+$ in the region of 100 km. If a steric factor of the order of unity is assummed for this reaction, an activation energy of about 6 kcal should be expected, i.e.

$$\gamma_7 = 7.5 \times 10^{-11} \ T^{\frac{1}{2}} \ e^{-6000/RT} \ cm^3 sec^{-1} \tag{54}$$

7.- CONCLUSIONS

An attempt has been made to determine the ionic formation of the D region by adopting an origin [Nicolet and Aikin, 1960] due to the simultaneous effects of cosmic rays in the lower D region with the photoionization of nitric oxide by Lyman-α plus a variable contribution from X-rays of $\lambda < 10$ A for the main part of the D-region which is below the mesopause level (near 85 km). The charge transfer process transforming N_2^+ into O_2^+ leads to a general deduction about processes involving O_2^+ ions and the determination of the ratio $n^+(NO)/n^+(O_2)$. By studying the vertical distribution of this ratio it has been shown that all the O_2^+ and N_2^+ ions produced by cosmic rays in the lower D region (altitude $\leq$ 70 km) are transformed into nitric oxide ions, i.e. equation (38),

$$q_{CR}(N_2^+, O_2^+) = (\alpha_D + \lambda \alpha_i) n^+(NO) n_e = [\alpha_i + \alpha_D/\lambda][n^+(NO)]^2 \tag{55}$$

In the main D region, there must be an increase of the ratio $n^+(O_2)/n^+(NO)$ with height which is limited by the direct photoionization of nitric oxide. Equations (32) and (33) can be simplified as

$$\alpha_{NO} n^+(NO) n_e = n(NO) \ I_{NO} + n^+(O_2) \ [\gamma_5 \ n(NO) + \gamma_7 \ n(O_2)] \tag{56}$$

and

$$\alpha_{NO} n^+(NO) n_e + \alpha_{O_2} n^+(O_2) n_e = n(N_2) \ I_{N_2} + n(O) I_O + n(O_2) I_{O_2} + n(NO) I_{NO} \tag{57}$$

These two equations suggest that any disturbance due to an increase of solar X-ray emission affects the ratio $n^+(O_2)/n^+(NO)$ in a complicated way since it always involves an increase of ionic reactions containing molecular oxygen ions. A corresponding increase of NO should be observed, particularly near the mesopause.

In the E layer, (57) remains a satisfactory expression for the total ionization. However, the subsidiary effect of atomic oxygen ions cannot be neglected, particularly in the upper part of the E layer, and instead of (56), the more general equation (33) must be used,

$$\alpha n^+(NO)n_e = n(NO)I_{NO} + n^+(O_2)[\gamma_5 n(NO) + \gamma_7 n(N_2)] + n^+(O)[\gamma_1 n(N_2) + \gamma_3 n(NO)]$$

$$(58)$$

This ionization equation along with the general equation (44) giving $n(NO)$ shows that there must be an ion-atom interchange process between O_2^+ and N_2. The existence of such a reaction implies a substantial increase of nitric oxide in the E layer compared with its photochemical value. This idea has been elaborated upon in order to explain how, above 85 km, a total content of the order of 10^{14} NO molecules cm^{-2} [Barth, 1964] and an emission of the order of 10^9 photons $cm^{-2} sec^{-1}$ [Krassovsky et al., 1962] in the continuum ($\lambda > 4000$ A) of the night airglow are related to ionospheric processes in the E layer.

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