

## Ionospheric Processes and Nitric Oxide

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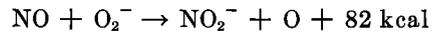
*Abstract.* Analysis of ionic processes in the ionosphere leads to the conclusion that nitric oxide and its ion are produced by a reaction between nitrogen molecules and molecular oxygen ions. Such a process implies a substantial increase of nitric oxide in the *E* layer to a value greater than the photochemical 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.

*Introduction.* The theory of the origin of the *D* region in the terrestrial ionosphere proposed by Nicolet and Aikin [1960] indicates that the lower part results from cosmic rays ionizing molecular oxygen and nitrogen and from solar Lyman  $\alpha$  ionizing nitric oxide during quiet solar conditions. The contribution of solar X rays at wavelengths 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.

If the origin of the normal *D* region is well known, however, the problem of its structure is far from being understood owing to the lack of information about 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 nighttime *D* region still depends on the theoretical investigations of the physical processes involving positive and negative ions.

Reid's [1964] excellent analysis of the present knowledge shows how the role of negative ions is important. The uncertainty about the extent to which laboratory measurements can be applied to the formation of the *D* region is clearly

seen in Branscomb's [1964] review of the negative ion reactions. 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 behavior 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:



A recent discussion of the various positive and negative ionic processes by Whitten and Popoff [1964] shows how ambiguities can 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  $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ . 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  $\alpha_D \approx 2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  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 recombina-

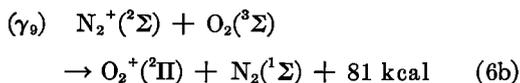
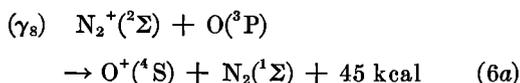
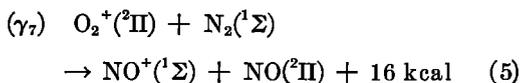
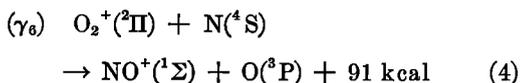
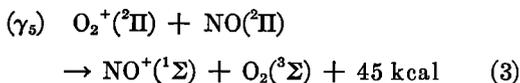
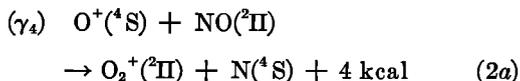
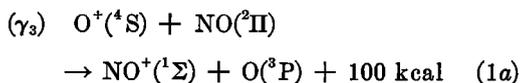
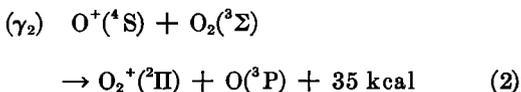
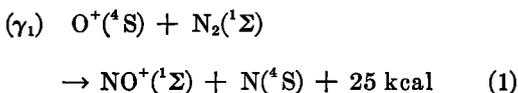
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tion is concerned, a value of the same order  $\alpha_4 = 2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  for  $\text{O}_2^+ + \text{O}_2^-$  and  $\text{NO}^+ + \text{NO}_2^-$  can be adopted without any experimental evidence. Other values such as  $\alpha_4 = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$  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.

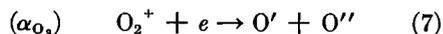
The purpose of the present paper is not, however, to review all the information available from laboratory experiments and aeronomic calculations, but to consider certain new aspects of the problem of nitric oxide production and related ionospheric studies. The analyses of recent spectrometric observations by *Barth* [1964] of nitric oxide and the mass-spectrometric studies by *Narcisi and Bailey* [1965] 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, 1965*].

*Ionic reactions and ionization equilibrium.* The various ionic reactions have been recently considered [*Nicolet and Swider, 1963*], and Figure 1 gives a general idea of the relationships between the various processes. Only the  $\text{NO}^+$  ion disappears by dissociative recombination alone, whereas  $\text{O}_2^+$  and  $\text{N}_2^+$  are subject to ion-atom interchange reactions and to charge transfer processes, respectively. The atomic ion  $\text{O}^+$  is transformed into molecular ions by ion-atom interchange reactions. The essential exothermic processes which are considered here are as follows:



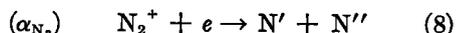
Reactions 1 and 5 producing  $\text{NO}^+$  ( $v'' \leq 3$ ) and  $\text{NO}^+$  ( $v'' \leq 2$ ), respectively, may correspond to luminescent reactions:  $\Delta v = 1$  near  $4.3 \mu$ ,  $\Delta v = 2$  near  $2.15 \mu$ , and  $\Delta v = 3$  near  $1.5 \mu$ .

The loss processes 1 and 2 of  $\text{O}^+$  are the only ones to be considered; their rate coefficients  $\gamma_1$  and  $\gamma_2$  are about  $10^{-12\text{--}11} \text{ cm}^3 \text{ sec}^{-1}$ . Reaction 5 is a loss process of  $\text{O}_2^+$  with a low rate coefficient for which we adopt  $\gamma_7 = 10^{-16\text{--}11} \text{ cm}^3 \text{ sec}^{-1}$ . The loss rate of  $\text{O}_2^+$  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



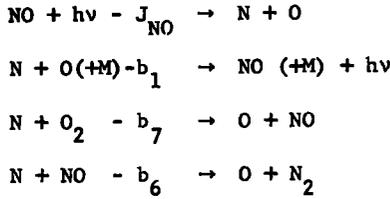
which leads to oxygen atoms in  $^3\text{P}$ ,  $^1\text{D}$ , and  $^1\text{S}$  states.

As far as the charge transfers (equation 6) are concerned, they are rapid enough to be the essential loss processes of  $\text{N}_2^+$  in the *D* and *E* regions. The dissociative recombination process



which may lead to nitrogen atoms in  $^4\text{S}$ ,  $^3\text{D}$ , and  $^2\text{P}$  states, is relatively important only in the *F* region.

C H E M O S P H E R E



I O N O S P H E R E

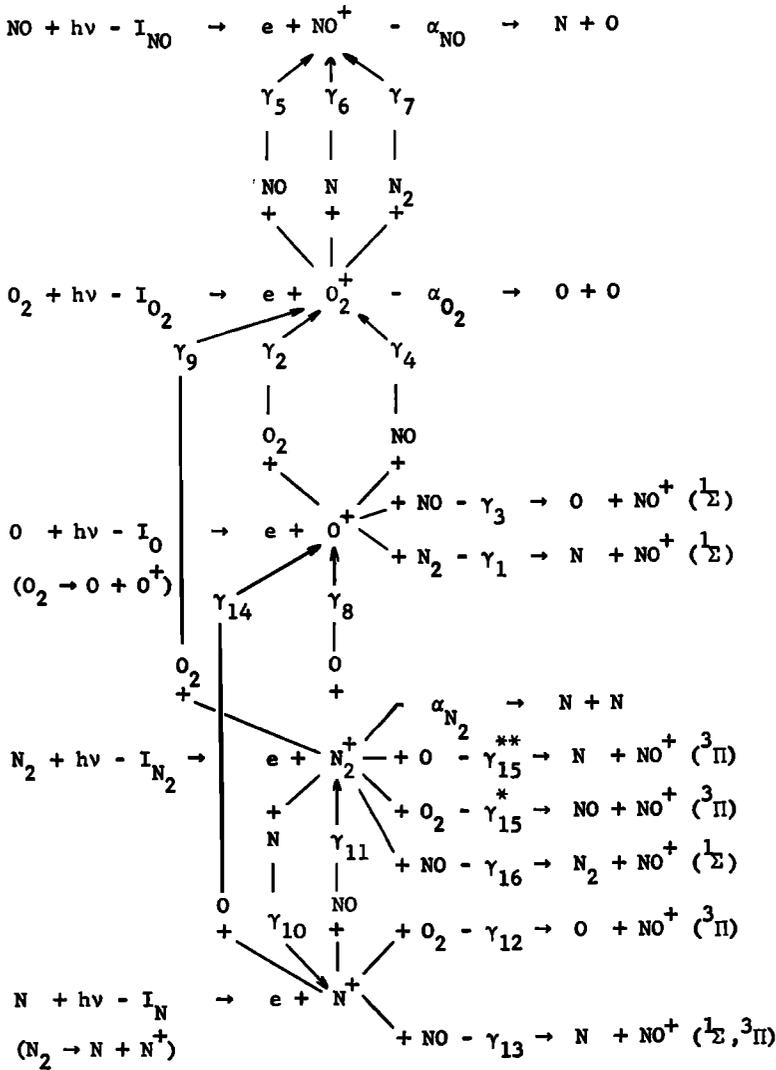
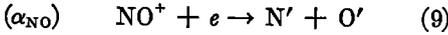


Fig. 1. Nitric oxide reactions.

The dissociative recombination of NO<sup>+</sup>



is the only loss process of this ion. It may give nitrogen atoms in <sup>4</sup>S and <sup>2</sup>D states and oxygen atoms in <sup>3</sup>P and <sup>1</sup>D states.

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

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

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

The negative ions of first importance are the molecular ions O<sub>2</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> 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 to be equal to the dissociative recombination coefficient

$$\alpha_i = \alpha_D \simeq 2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1} \quad (11a)$$

but not smaller than

$$\alpha_i \geq 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \quad (11b)$$

If *I*<sub>N<sub>2</sub></sub>, *I*<sub>O<sub>2</sub></sub>, *I*<sub>O</sub>, and *I*<sub>NO</sub> are the photoionization rate coefficient of N<sub>2</sub>, O<sub>2</sub>, 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

$$n^+(N_2) = \frac{n(N_2)I_{N_2}}{\gamma_3 n(O) + \gamma_6 n(O_2) + (\alpha_{N_2} + \lambda \alpha_i) n_e} \quad (12)$$

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

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

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

*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,

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

A production of nitric oxide comes from

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

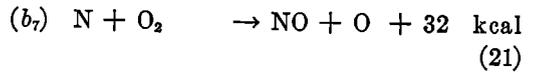
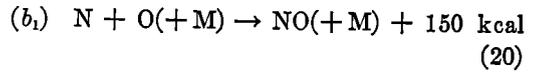
These productions of N and NO by ionic reactions must be added to chemical production [Nicolet, 1965] by

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

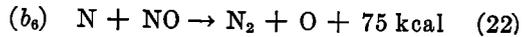
corresponding to the photodissociation of NO and N<sub>2</sub>, and

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

corresponding to the reactions



The common loss process



combines with (20) and (21) as

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

and

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

Using the ionization equilibrium equations 12 to 15 which can be applied to the D, E, and F<sub>1</sub> layers, plus the chemical reactions, the following expressions are obtained for NO and N, neglecting the term λ α<sub>i</sub> n<sup>+</sup>(NO) n<sub>e</sub>.

$$\left[ \frac{dn(NO)}{dt} \right] + n(NO) [J_{NO} + I_{NO}$$

$$\begin{aligned}
 &+ b_6 n(\text{N}) + (\gamma_3 + \gamma_4) n^+(\text{O}) + \gamma_5 n^+(\text{O}_2)] \\
 = &n(\text{N})[b_1 n(\text{O}) + b_7 n(\text{O}_2)] + \gamma_7 n^+(\text{O}_2) n(\text{N}_2) \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 [dn(\text{N})/dt] + n(\text{N})[b_1 n(\text{O}) \\
 + b_6 n(\text{NO}) + b_7 n(\text{O}_2)] \\
 = &n(\text{NO})[J_{\text{NO}} + I_{\text{NO}} + (\gamma_3 + \gamma_4) n^+(\text{O}) \\
 + &\gamma_3 n^+(\text{O}_2)] + n(\text{N}_2)[2J_{\text{N}_2} + 2\gamma_1 n^+(\text{O}) \\
 + &\gamma_7 n^+(\text{O}_2)] + 2\alpha_{\text{N}_2} n^+(\text{N}_2) n_e \quad (26)
 \end{aligned}$$

The conditions for the simultaneous variation of  $n(\text{NO})$  and  $n(\text{N})$  can be conveniently written, from (25) and (26), as

$$\begin{aligned}
 \frac{dn(\text{NO})}{dt} + \frac{dn(\text{N})}{dt} + 2b_6 n(\text{NO})n(\text{N}) \\
 = &2n(\text{N}_2)[J_{\text{N}_2} + \gamma_7 n^+(\text{O}_2) + \gamma_1 n^+(\text{O})] \\
 + &2\alpha_{\text{N}_2} n^+(\text{N}_2) n_e \quad (27)
 \end{aligned}$$

For equilibrium conditions, (27) leads to

$$\begin{aligned}
 b_6 n(\text{NO})n(\text{N}) = &n(\text{N}_2)[J_{\text{N}_2} + \gamma_7 n^+(\text{O}_2) \\
 + &\gamma_1 n^+(\text{O})] + \alpha_{\text{N}_2} n^+(\text{N}_2) n_e \quad (28)
 \end{aligned}$$

or

$$\begin{aligned}
 n(\text{N})[b_1 n(\text{O}) + b_7 n(\text{O}_2)] \\
 = &n(\text{N}_2)[J_{\text{N}_2} + \gamma_1 n^+(\text{O})] \\
 + &n(\text{NO})[J_{\text{NO}} + I_{\text{NO}} + (\gamma_3 + \gamma_4) n^+(\text{O}) \\
 + &\gamma_3 n^+(\text{O}_2)] \quad (29)
 \end{aligned}$$

The effect of ionic reactions on N and NO concentrations is easy to understand, as the terms with the symbol gamma correspond to the ionospheric production of atomic nitrogen or nitric oxide.

*Ionospheric conditions in various ionospheric layers.* Equations 12 to 15 lead to the general ionization for steady-state conditions

$$\begin{aligned}
 n(\text{N}_2)I_{\text{N}_2} + n(\text{O})I_{\text{O}} + n(\text{O}_2)I_{\text{O}_2} + n(\text{NO})I_{\text{NO}} \\
 = &n_e \{n^+(\text{N}_2)[\alpha_{\text{N}_2} + \lambda\alpha_1] + n^+(\text{O}_2)[\alpha_{\text{O}_2} + \lambda\alpha_1] \\
 + &n^+(\text{NO})[\alpha_{\text{NO}} + \lambda\alpha_1]\} \quad (30)
 \end{aligned}$$

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

The essential characteristics of the loss processes for  $\text{N}_2^+$  ions is the competition between

charge transfer and dissociative recombination. The absence of  $\text{N}_2^+$  ions in the E layer is due to the effect of charge transfer. Assuming that the  $\text{N}_2^+$  loss in the D region by dissociative recombination is inappreciable compared with other processes, (12) becomes

$$n^+(\text{N}_2)[\gamma_8 n(\text{O}_2) + \gamma_9 n(\text{O})] = Xn(\text{N}_2)I_{\text{N}_2} \quad (31)$$

where  $X = 1$ . The parameter  $0 \leq X \leq 1$  reaches its minimum value in the F<sub>2</sub> layer; it can be taken as unity in the D and E layers and is still about 1 in the F<sub>1</sub> layer. This leads to a simplification of (30) for the lower ionospheric layers where we are considering the behavior of production of NO and NO<sup>+</sup>. Equation 30 can be conveniently written as follows:

$$\begin{aligned}
 Xn(\text{N}_2)I_{\text{N}_2} + n(\text{O})I_{\text{O}} + n(\text{O}_2)I_{\text{O}_2} + n(\text{NO})I_{\text{NO}} \\
 = &n_e \{n^+(\text{O}_2)[\alpha_{\text{O}_2} + \lambda\alpha_1] + n^+(\text{NO})[\alpha_{\text{NO}} + \lambda\alpha_1]\} \quad (32)
 \end{aligned}$$

where  $X = 1$ .

It is natural to compare (32) with the ionization equation (15) related to NO<sup>+</sup>:

$$\begin{aligned}
 n_e n^+(\text{NO})[\alpha_{\text{NO}} + \lambda\alpha_1] \\
 = &n^+(\text{O}_2)[\gamma_8 n(\text{N}) + \gamma_7 n(\text{N}_2)] \\
 + &n^+(\text{O})\gamma_1 n(\text{N}_2) n(\text{NO})[I_{\text{NO}} + \gamma_3 n^+(\text{O}) \\
 + &\gamma_3 n^+(\text{O}_2)] \quad (33)
 \end{aligned}$$

At sufficiently high altitudes the first term on the right of (33) certainly becomes negligible and the presence of NO<sup>+</sup> ions depends on the direct photoionization and especially on the reactions involving the atomic oxygen ion. An attempt at determining the concentration of NO<sup>+</sup> 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<sup>+</sup> concentration is comparable to that of O<sub>2</sub><sup>+</sup>, the reaction between O<sub>2</sub><sup>+</sup> and N<sub>2</sub> 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

$$n_e n^+(\text{NO})[\alpha_{\text{NO}} + \lambda\alpha_i] = n^+(\text{O}_2)[\gamma_5 n(\text{NO}) + \gamma_6 n(\text{N}) + \gamma_7 n(\text{N}_2)] \quad (34)$$

and, since atomic nitrogen does not exist in sufficient quantity,

$$\frac{n_e n^+(\text{NO})}{n^+(\text{O}_2)} = \frac{\gamma_7 n(\text{N}_2) + \gamma_5 n(\text{NO})}{\alpha_{\text{NO}} + \lambda\alpha_i} \quad (35)$$

which is the proper ionization equation to apply below the region where Lyman  $\alpha$  ionizes NO.

Taking  $\alpha_{\text{NO}} + \lambda\alpha_i \approx \alpha_{\text{O}_2} + \lambda\alpha_i$  in the general equation (32) and representing the production processes by  $q$ , we write

$$q = (1 + \lambda)(\alpha_D + \lambda\alpha_i)n_e^2 \quad (36)$$

Introducing (36) in (35), we obtain the ratio

$$\frac{n^+(\text{NO})}{n^+(\text{O}_2)} = \frac{\gamma_7 n(\text{N}_2) + \gamma_5 n(\text{NO})}{[(\alpha_D + \lambda\alpha_i)q/(1 + \lambda)]^{1/2}} \quad (37)$$

if  $\text{NO}^+$  is the principal ion.

At 60 km, where only ionization by cosmic rays occurs during the normal daytime and nighttime conditions,  $n^+(\text{NO}) \gg n^+(\text{O}_2)$ , and (36) is equivalent to

$$q = (\alpha_D + \lambda\alpha_i)n^+(\text{NO})n_e \\ = [\alpha_i + \alpha_D/\lambda][n^+(\text{NO})]^2 \quad (38)$$

With a cosmic ray production of not less than  $5 \times 10^{-8}$  ions  $\text{cm}^{-3} \text{sec}^{-1}$ , the time to reach equilibrium conditions is always less than one hour.

Exact ionospheric conditions cannot presently be determined, since the rate coefficient  $\gamma_7$  is not known. A value  $\gamma_7 = 10^{-26.21}$  can be adopted if  $\text{O}_2^+$  has to be eliminated in the lower  $D$  region. This process has not been observed in the laboratory owing 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  $\text{O}_2^+$  at 65 km with a ratio  $n(\text{NO}^+)/n^+(\text{O}_2)$  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- $\alpha$  intensity, could favor such a vertical ionic distribution.

It could be claimed, however, that in the  $E$  layer, the process between  $\text{O}_2^+$  and  $\text{N}_2$  is negligible

and, hence, that it is not responsible for the presence of  $\text{NO}^+$ . Nevertheless, such a conclusion is premature. Thus, finding in observational data [*Holmes et al.*, 1965] that  $n^+(\text{NO}) \approx n^+(\text{O}_2)$  in the daytime  $E$  layer, we find that at 100 km equation 33 leads to

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

As a result, we are led to consider that a process like  $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$  or  $n(\text{NO}) I_{\text{NO}}$  is, in fact, important. If  $n(\text{NO})$  is  $10^9 \text{ cm}^{-3}$  or less, the direct photoionization is then less than  $50 \text{ cm}^{-3} \text{sec}^{-1}$ . The best attempt at determining a production of more than 100  $\text{NO}^+$  ions  $\text{cm}^{-3} \text{sec}^{-1}$  at 100 km would be to consider a very small concentration of  $\text{O}^+$  ions. The X-ray production would always be the essential process.

To obtain information on the existence of the reaction process  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$ , it is perhaps necessary to consider nighttime conditions in the  $E$  layer. In view of the observational results obtained for the nighttime  $E$  layer [*Holmes et al.*, 1965], we can put forward the hypothesis that the ratio  $n^+(\text{NO}) > n^+(\text{O}_2)$  depends on the ion-interchange process, i.e.

$$\gamma_5 n(\text{NO}) + \gamma_7 n(\text{N}_2) + \gamma_{\text{O}_2} n_e \leq 10^{-3} \text{ sec}^{-1} \quad (40)$$

With  $n(\text{N}_2) \approx 10^{18}$  to  $10^{19} \text{ cm}^{-3}$  and  $\gamma_7 \approx 10^{-18}$  to  $10^{-15} \text{ cm}^3 \text{sec}^{-1}$ , consideration must be given to the process involving  $\text{O}_2^+$  and  $\text{N}_2$ . However, it is scarcely worth pursuing this at the 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,  $\gamma_7 n^+(\text{O})$  or  $(\gamma_5 + \gamma_7) n^+(\text{O}_2)$ , 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  $\text{NO}^+$  ions is ion-atom interchange with atomic oxygen ions, the problem of explaining the whole situation becomes almost impossible. For example, assuming  $\alpha_{\text{NO}} \simeq \alpha_{\text{O}_2} = 2 \times 10^{-7} \text{ cm}^3 \text{sec}^{-1}$  and  $10^6$  electrons  $\text{cm}^{-3}$  at 100 km, equation 32 leads to

$$\alpha n_e^2 = q = 2000 \text{ electrons cm}^{-3} \text{sec}^{-1} \quad (41)$$

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

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

and

$$\alpha n^+(NO)n_e = \gamma_1 n^+(N_2)n^+(O) \quad (42b)$$

To attain a ratio  $n^+(NO)/n^+(O_2) \approx 1$ , it would be necessary to assume that the electron production by atomic oxygen is at least 50% 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 needed.

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

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

*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 that can be conveniently written as follows:

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

$$\frac{n(N_2)[J_{N_2} + \gamma_1 n^+(O) + \gamma_7 n^+(O_2)]}{n(N_2)[J_{N_2} + \gamma_1 n^+(O)] + n(NO)[J_{NO} + I_{NO} + (\gamma_3 + \gamma_4)n^+(O) + \gamma_5 n^+(O_2)]} \quad (44)$$

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

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

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

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

since the ion-atom interchange process in which  $O^+$  is involved increases rapidly with altitude.  $n^*(NO)$  corresponds to the photochemical equilibrium value given by [Nicolet, 1965],

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

with the following requirement

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

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

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

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

$$n^2(NO) = n^*(NO) \cdot \frac{n(N_2)[J_{N_2} + \gamma_1 n^+(O) + \gamma_7 n^+(O_2)]}{J_{NO} + I_{NO} + [\gamma_3 + \gamma_4]n^+(O) + \gamma_5 n^+(O_2)} \quad (50a)$$

and

$$n^2(\text{NO}) \approx n^*(\text{NO}) \frac{n(\text{N}_2)[J_{\text{N}_2} + \gamma_1 n^+(\text{O}) + \gamma_7 n^+(\text{O}_2)]}{J_{\text{NO}} + I_{\text{NO}}} \quad (50b)$$

which leads to

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

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

$$n^*(\text{NO}) \approx 10^6 \text{ cm}^{-3} \quad n(\text{N}_2) \approx 10^{13} \text{ cm}^{-3}$$

$$J_{\text{NO}} + I_{\text{NO}} \approx 5 \times 10^{-7} \text{ sec}^{-1}$$

equation 50b leads to

$$n(\text{NO}) = 5 \times 10^{12} [J_{\text{N}_2} + \gamma_1 n^+(\text{O}) + \gamma_7 n^+(\text{O}_2)]^{1/2} \text{ cm}^{-3} \quad (52)$$

Any value of a rate coefficient in the bracket of (52) not less than  $4 \times 10^{-14} \text{ sec}^{-1}$  leads to  $n(\text{NO}) > n^*(\text{NO}) = 10^6 \text{ cm}^{-3}$ , that is a value greater than the photochemical value. If the rate coefficient  $\gamma_7 n^+(\text{O}_2)$  reaches values between  $10^{-11}$  and  $10^{-10} \text{ sec}^{-1}$ , the nitric oxide concentration is between  $2 \times 10^7$  and  $5 \times 10^7 \text{ cm}^{-3}$ .

An attempt can be made to determine the vertical distribution of NO for photoionization equilibrium conditions. Because of the lack of information about the ratio  $n^+(\text{NO})/n^+(\text{O}_2)$  between 85 km and 110 km, we assume that the electron concentration increases from  $2.5 \times 10^8 \text{ cm}^{-3}$  at 85 km to  $10^6 \text{ cm}^{-3}$  at 90 km and  $1 \times 10^5$  at 100 km with a rate coefficient  $10^{-10} n_e \text{ sec}^{-1}$  instead of  $\gamma_7 n^+(\text{O}_2) \text{ sec}^{-1}$ . With such a hypothesis, an approximate form of the vertical distribution can be obtained. Figure 2 illustrates the effect of the production of NO by the reaction between  $\text{O}_2^+$  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  $n(\text{NO})$  is about  $10^7 \text{ cm}^{-3}$  and, with a thickness of about 30 km, the total

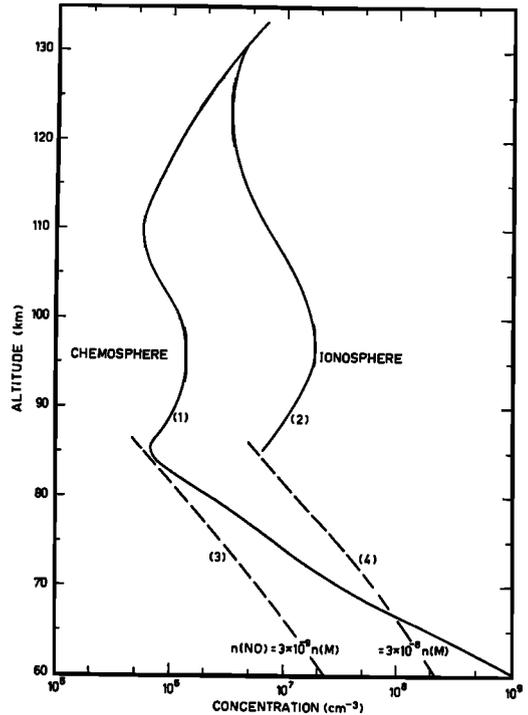


Fig. 2. Vertical distribution of nitric oxide. (1) photoequilibrium conditions in the chemosphere; (2) photoequilibrium conditions in the ionosphere; (3) and (4) mixing conditions.

content is not less than  $5 \times 10^{13}$  molecules  $\text{cm}^{-2}$ . Since Barth [1964] gives  $1.7 \times 10^{14} \text{ cm}^{-2}$  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  $n(\text{NO}) = 3 \times 10^{-9} n(\text{M})$  and  $3 \times 10^{-8} n(\text{M})$  shown in Figure 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 very complicated, since the lifetime of NO is not short between 65 and 85 km. In treating nonequilibrium cases we have to consider different ionization conditions (intensity and duration) to relate the equilibrium concentrations to the rate of production of NO, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup>. 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<sup>+</sup> 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  $1.7 \times 10^{14}$  molecules cm<sup>-2</sup> for the column density of nitric oxide above 85 km, the values of  $n(\text{NO})$  in Figure 2 should be multiplied by a factor of only 3 to give the same total content.

*Nitric oxide and the airglow continuum.* Several authors have suggested that



contributes to the airglow continuum [Krassovskiy, 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  $6.4 \times 10^{-17}$  cm<sup>3</sup> sec<sup>-1</sup> ob-

tained by Fontijn *et al.* [1964] with the following division— $3.2 \times 10^{-17}$  cm<sup>3</sup> sec<sup>-1</sup> for  $\lambda < 7250$  Å and  $\lambda > 7250$  Å [Nicolet, 1965]—it is possible to make a comparison with the observed value of the airglow continuum. An approximate value of about  $6 \times 10^9$  photons cm<sup>-2</sup> sec<sup>-1</sup> is given [Krassovskiy *et al.*, 1962] for the spectral range 4000–7000 Å.

With the NO vertical distribution shown in Figure 2 and approximate concentrations of atomic oxygen for nighttime conditions, it is possible to determine the general emission of the continuum. The result is illustrated in Figure 3, which gives the number of photons cm<sup>-2</sup> sec<sup>-1</sup> between 75 km and 115 km. The total emission corresponds to  $3.4 \times 10^9$  photons cm<sup>-2</sup> sec<sup>-1</sup>, or  $1.7 \times 10^9$  photons cm<sup>-2</sup> sec<sup>-1</sup> for the 4000–7250 Å range. Normalizing to the observed value, the theoretical flux should be multiplied by a factor of about 3 to give the same number of photons cm<sup>-2</sup> sec<sup>-1</sup>. This is the same factor that was used to obtain the total number of NO molecules observed by Barth [1964]. This may be pure coincidence. Nevertheless, this factor corresponds to an average value of  $3 \times 10^{-16}$  cm<sup>3</sup> sec<sup>-1</sup> for the rate coefficient of the reaction O<sub>2</sub><sup>+</sup> + N<sub>2</sub> → NO + NO<sup>+</sup> in the region of 100 km. If a steric factor of the order of unity is assumed for this reaction, an activation energy of about 6 kcal should be expected, i.e.

$$\gamma_7 = 7.5 \times 10^{-11} T^{1/2} e^{-6000/RT} \text{ cm}^3 \text{ sec}^{-1} \quad (54)$$

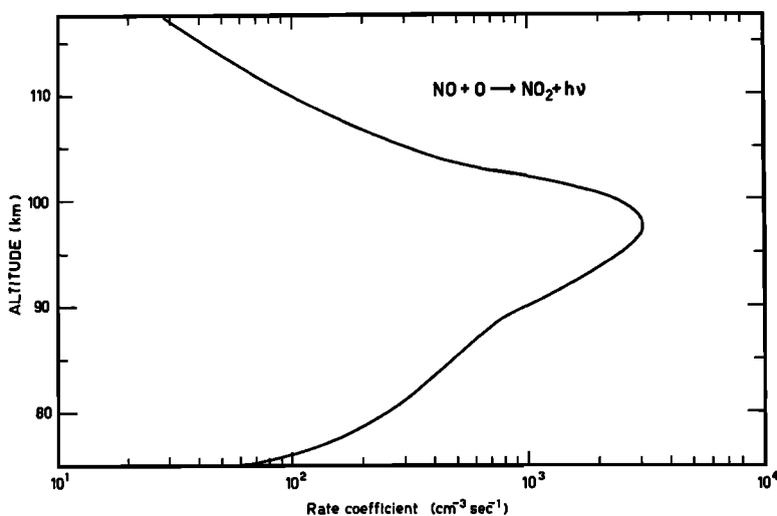


Fig. 3. Number of photons  $\lambda > 4000$  Å cm<sup>-2</sup> sec<sup>-1</sup>.

*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  $\alpha$  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  $n^+(\text{NO})/n^+(\text{O}_2)$ . 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 (equation 38):

$$q_{CR}(N_2^+, O_2^+) = (\alpha_D + \lambda\alpha_n)n^+(\text{NO})n_e \quad (55)$$

$$= [\alpha_i + \alpha_D/\lambda][n^+(\text{NO})]^2$$

In the main *D* region, there must be an increase of the ratio  $n^+(\text{O}_2)/n^+(\text{NO})$  with height which is limited by the direct photoionization of nitric oxide. Equations 32 and 33 can be simplified as

$$\alpha_{NO}n^+(\text{NO})n_e = n(\text{NO})I_{NO}$$

$$+ n^+(\text{O}_2)[\gamma_5n(\text{NO}) + \gamma_7n(\text{O}_2)] \quad (56)$$

$$\alpha_{NO}n^+(\text{NO})n_e + \alpha_{O_2}n^+(\text{O}_2)n_e = n(N_2)I_{N_2}$$

$$+ n(\text{O})I_{\text{O}} + n(\text{O}_2)I_{\text{O}_2} + n(\text{NO})I_{NO} \quad (57)$$

These two equations suggest that any disturbance due to an increase of solar X-ray emission affects the ratio  $n^+(\text{O}_2)/n^+(\text{NO})$  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 (33) must be used:

$$\alpha n^+(\text{NO})n_e$$

$$= n(\text{NO})I_{NO} + n^+(\text{O}_2)[\gamma_5n(\text{NO}) + \gamma_7n(N_2)]$$

$$+ n^+(\text{O})[\gamma_1n(N_2) + \gamma_3n(\text{NO})] \quad (58)$$

This ionization equation along with the general equation 44 giving  $n(\text{NO})$  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  $\text{cm}^{-3}$  [Barth, 1964] and an emission of the order of  $10^9$  photons  $\text{cm}^{-2} \text{sec}^{-1}$  [Krassovsky et al., 1962] in the continuum ( $\lambda > 4000$  A) of the night airglow are related to ionospheric processes in the *E* layer. With regard to the nighttime *E* layer, there is a possibility of obtaining electron densities of the order of  $10^8$  electrons  $\text{cm}^{-3}$  resulting from the ionization of nitric oxide by Lyman  $\alpha$ .

*Acknowledgment.* This work was supported by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Massachusetts, under contract AF 19(268)4014 and in part by the National Science Foundation under grant GP 2914.

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(Manuscript received October 30, 1964.)