Planet. Space Sci. 1963, Vol. 11, pp. 1459 to 1482. Pergamon Press Ltd. Printed in Northern Ireland

IONOSPHERIC CONDITIONS*

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(*Received* 31 *July* 1963)

Abstract—A general analysis of ionospheric conditions has been made in the light of possible ionic reactions occurring in the upper atmosphere. Data obtained on various parameters, such as ionic production and recombination, show that precise knowledge of the spectral distribution of solar radiation is needed and that other experimental determinations on dissociative recombinations are required.

The ionic complexity of the ionosphere is underlined by describing how the atomic ions O^+ and N^+ react with N_2, O_2 and NO molecules. The behavior of the molecular ions N_2^+, O_2^+ and NO^+ depends on a group of simultaneous processes involving charge transfers and ion-atom interchanges which are more important than dissociative recombinations. The altitude distribution of ions is exemplified by discussing the relative importance of various loss coefficients in the *D*-, *E*- and *F*-regions. It is seen that molecular nitrogen ions are subject to important charge transfer processes, that nitric oxide ions are always final products destroyed only by dissociative recombination. Additionally, the entire production of atomic oxygen ions is related to the photoionization of molecular nitrogen. Some information is also given on possible anomalies in the ratio of O_2^+ and NO^+ densities in the lower ionosphere. From the lack of sufficient experimental information on ionic processes it is shown that a precise analysis of ionospheric behavior remains highly speculative.

1. INTRODUCTION

The problem of the interpretation of the physics of the ionosphere is in a state of confusion. Increasing knowledge of the solar spectrum in the far ultraviolet has, apparently, not as yet lead to a consistent picture of photoionization processes in the ionosphere. While Hinteregger and Watanabe(1) have determined a certain distribution of the number of photons available at the top of the ionosphere, Ivanov-Kholodny(2) has adopted another distribution. The data of Table 1 between 900 and 30 Å show that the difference is important. It is clear that for $\lambda < 800$ Å, the number of photons used by Ivanov-Kholodny is ten times that obtained by Hinteregger and Watanabe. Nevertheless, Norton, Van Zandt and Denison(3) using the spectral distribution given by Hall, Damon and Hinteregger(4), and Ivanov-Kholodny(2) claim that they have satisfactorily interpreted the ionospheric structure.

It is difficult to understand how it is possible to make such divergent interpretations of optional ionospheric behavior even allowing for variation of the far ultraviolet spectrum with solar activity. Analysis of the solar spectrum in the region of $\lambda > 800$ by Detweiler, Garrett, Purcell and Tousey(5) and by Zirin, Hall and Hinteregger(6) shows consistent results. In the spectral region of $\lambda < 800$, Table 1 indicates a difference of a factor of 10 which will affect the ionization of all thermospheric constituents, namely N_2, O_2 and O. Such a variation cannot exist in the whole ultraviolet spectrum of wavelengths $\lambda \geq 800$ Å, even for the maximum-to-minimum variation of the solar cycle.

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* Presented at the Fourth International Space Science Symposium of COSPAR, Warsaw, June 1963.
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TABLE 1. NUMBER OF PHOTONS ($cm^{-2}sec^{-1}$) AVAILABLE AT THE TOP OF THE EARTH'S ATMOSPHERE ACCORDING TO HINTEREGGER-WATANABE (H-W) AND IVANOV-KHOLODNY (I-K)

$\Delta\lambda$	910–850	850–800	800–700	700–500 Å
(H-W)	$9{\cdot}5 \times 10^{9}$	$2{\cdot}5 \times 10^{9}$	$5{\cdot}0 \times 10^{9}$	$4{\cdot}7 \times 10^{9}$ photons
(I-K)	$5{\cdot}0 \times 10^{9}$	$2{\cdot}1 \times 10^{9}$	$4{\cdot}4 \times 10^{10}$	$3{\cdot}2 \times 10^{10}$ photons

$\Delta\lambda$	600–500	500–400	400–300	300–230 Å
(H-W)	$5{\cdot}9 \times 10^{9}$	$2{\cdot}4 \times 10^{9}$	$7{\cdot}2 \times 10^{9}$	$3{\cdot}1 \times 10^{9}$ photons
(I-K)	$4{\cdot}9 \times 10^{10}$	$3{\cdot}0 \times 10^{10}$	$9{\cdot}6 \times 10^{10}$	$5{\cdot}3 \times 10^{10}$ photons

$\Delta\lambda$	230–170	170–11r	110–80	806–0	60–30 Å
(H-W)	$3{\cdot}3 \times 10^{9}$	$3{\cdot}5 \times 10^{9}$	$2{\cdot}4 \times 10^{8}$	$1{\cdot}8 \times 10^{8}$	$1{\cdot}6 \times 10^{8}$ photons
(I-K)	$2{\cdot}4 \times 10^{10}$	$5{\cdot}7 \times 10^{9}$	$2{\cdot}24 \times 10^{9}$	$1{\cdot}1 \times 10^{9}$	$8{\cdot}4 \times 10^{8}$ photons

On the other hand, Hinteregger(7), and Norton *et al.*(3) consider an atmospheric model with an atomic oxygen concentration which is not less than four times the molecular oxygen concentration at 110 km and not less than the molecular nitrogen concentration at 130 km. Denison and Van Zandt(3) claim that Nicolet's model(8) is inconsistent with the data of Hall *et al.*(4) This deduction by Hinteregger(7) and Norton *et al.*(3) is based essentially on the behavior of two solar lines, namely Lγ at 972 Å and Si III at 1206 Å in the wing of Lyman-α. However, such a deduction can be modified if the laboratory measurements of the absorption cross-sections are not adapted to the atmospheric absorption. As an example, the vertical distribution of solar photons for Lyman-γ at 972·537 Å for an absorption cross-section of the order of 1×10^{-16} cm^2 using Nicolet's model fits the vertical distribution deduced by Hall *et al.*(4) An N_2 band with a head at 972·2 Å, which is shaded toward longer wavelengths, has more than 10 rotational lines in a narrow spectral range with $J_p(15) = 973{\cdot}98$ Å. The absorption cross-section depends on the distribution of the rotational lines between 972 Å and 974 Å and a high resolution spectrum is needed to determine the exact absorption cross-section of λ 972·537 Å. It cannot be claimed that the cross-section is 1×10^{-16} cm^2 or 3×10^{-16} cm^2 without a special analysis of laboratory and atmospheric conditions. It is evident that an observation of solar Lγ free from atmospheric absorption is required to make a correct measurement of the exact photon flux at the top of the Earth's atmosphere.

Hinteregger's data(7) show several anomalies. The ratio $n(N_2)/n(O_2)$ decreases from a factor of 10 at 120 km to 4 and 2·5 at 130 km and 150 km; respectively. The ratio $n(O)/n(O_2)$ decreases from about 15 between 110 and 120 km to 10 at 130 km and 140 km. The normal behavior for such ratios is to increase with height. Furthermore, it should be noted that Hinteregger gives the ratio $n(N_2)/n(O)$ equal to only 0·4 at 130 km while the ratio $n(O)/n(O_2)$ reaches at least 15 between 110 km and 120 km. On the other hand Denison and Van Zandt(3) using the same observational data adopt the following ratios: $n(O)/n(O_2) = 4$ at 110 km, 9 at 120 km and about 15 at 130 km where $n(O)$ almost reaches the concentration of $n(N_2)$.

Ratios such as $n(O)/n(N_2) \geq 1$ at 125 km do not agree with mass spectrometric measurements made in the U.S.A. (cf. Townsend(9), Schaefer(10)) and in the U.S.S.R. (cf. Pokhunkov(11)). Furthermore, an observation made by Schaefer shows that $n(O)/n(O_2) = 1$ near 118 km and not more than 3 at 130 km.

The description of the daytime ionospheric regions as given by Norton *et al.*(3) or by

Ivanov-Kholodny(2) cannot be used for night-time conditions without the addition of another process. Antonova and Ivanov-Kholodny(12) have introduced the ionization effect of electrons. The flux in the ionosphere should be at least of the order of 1 erg cm^{-2} sec^{-1} for electrons of energy between 100 eV and 10 keV, i.e. at least of the order of 5×10^9 electrons cm^{-2} sec^{-1} for an energy of 200 eV. In other words, Ivanov-Kholodny, after introducing a high ionization rate for daytime conditions, is obliged to consider a high recombination rate to obtain the observed electron concentrations. When a large recombination rate is used for night-time conditions it would destroy the *F2*-layer and a corpuscular flux is postulated to maintain a nocturnal ionosphere. However, such an electron flux would excite the night airglow spectrum in such a way that auroral emissions should occur; in particular the first negative system, and the first positive system of nitrogen. Since these emissions are not observed it can be concluded, as Galperin(13) has shown, that the normal corpuscular flux is very small. It is practically negligible compared with the ultraviolet flux, which is certainly greater than 1 erg cm^{-2} sec^{-1}, and is insignificant compared with the 15 ergs claimed by Ivanov-Kholodny as the normal ultraviolet flux of $\lambda = 900$ Å.

A recent analysis shows how a corpuscular flux must be considered. At mid-latitudes over North America, O'Brien(14) has measured, at 1000 km, a flux of precipitated electrons of 10^3 and 10^4 cm^{-2} sec^{-1} for energies ≥ 40 keV. His discussion on the airglow excitation indicates that the normal fluxes are between 10^{-2} and 10^{-1} ergs cm^{-2} sec^{-1} for 1 keV electrons. It is possible that some anomaly could be detected as shown recently by Gledhill and Van Rooyen(15) using O'Brien's data(14).

The airglow data suggest various limits for the electron flux. An emission of the green line of atomic oxygen above 300 km, equal to the intensity of that of the normal airglow and due to the excitation of electrons of about 10 eV energy, would correspond to a flux of 10^{10} electrons cm^{-2} sec^{-1}. An electron flux in the energy range 50–500 eV, i.e. less than 1 keV, cannot be more than 10^7 electrons cm^{-2} sec^{-1} since it would lead to such an excitation of N_2^+ bands which are not observed in the airglow. Furthermore, the second positive system of nitrogen, which is likewise not observed in the airglow, requires the same limiting conditions for the electron flux. Therefore, the ionization rate coefficient for corpuscular radiation cannot be greater than 10^{-9} sec^{-1}, i.e. it is always less than 10^{-2} the photoionization rate coefficient. Since there is no possibility of finding a permanent electron flux in the night-time ionosphere greater than 0·1 erg cm^{-2} sec^{-1}, it must be concluded that the total ionization production by corpuscular radiation cannot attain, in the whole ionosphere (for normal conditions outside of the auroral zone), one hundredth of that produced by photoionization.

Finally, the number of atmospheric models used to explain upper-atmosphere behavior has added to the confusion and leads to other difficulties. Consequently, before trying to clarify the general problem, an attempt is made to show the complexity of the problem of ionospheric reactions and the difficulty of deducing a correct explanation of the ionosphere without an exact knowledge of the various physical parameters involved.

2. POSITIVE ION REACTIONS

Starting from the observational knowledge of the inosphere, the following positive ions must be considered: H^+, He^+, N^+, N_2^+, O^+, O_2^+, NO^+, Mg^+, Ca^+, ... etc. Further, it should be noted that metallic ions are not present in the whole ionosphere, H^+ and He^+ occur in the upper part of the ionosphere above the *F2*-peak, O_2^+, NO^+ and O^+ are the essential ionic constituents of the *D*-, *E*- and *F*-regions and N_2^+ and N^+ are minor ions with maximum concentrations in the *F*-region. Thus, O^+, N^+, NO^+, O_2^+ and N_2^+ must be considered as the basic ions which are involved in the various reactions.

The predominant ion in the *F*-region, O^+, is subject to the following ion-atom interchange reactions:

$$(\gamma_1);\ O^+(^4S) + N_2(^1\Sigma) \rightarrow NO^+(^1\Sigma) + N(^4S) + 1{\cdot}12\ \text{eV} \tag{1}$$

$$(\gamma_2);\ O^+(^4S) + O_2(^3\Sigma) \rightarrow O_2^+(^2\Pi) + O(^3P) + 1{\cdot}54\ \text{eV} \tag{2}$$

$$(\gamma_3);\ O^+(^4S) + NO(^2\Pi) \rightarrow NO^+(^1\Sigma) + O(^3P) + 4{\cdot}37\ \text{eV} \tag{3}$$

$$(\gamma_4);\ O^+(^4S) + NO(^2\Pi) \rightarrow O_2^+(^2\Pi) + N(^4S) + 0{\cdot}15\ \text{eV}. \tag{4}$$

The following charge transfer process must be added to reactions (1) to (4):

$$(\gamma_5);\ O^+(^4S) + O_2(^3\Pi) \rightarrow O_2^+(^2\Pi) + O(^3P) + 1{\cdot}54\ \text{eV}. \tag{5}$$

Since there is no practical way to distinguish between (2) and (5), process (5) will be ignored in the analysis. Similarly, a charge transfer process between O^+ and NO is equivalent to reaction (3).

The rate coefficients of the ion-atom interchange reactions (1) to (4) are not well known. The rate of (2) has been measured by Dickinson and Sayers(16), Langstroth and Hasted(17) and Fite, Rutherford, Snow and Van Lint(18). The following values have been obtained:

$$\gamma_2 \geq 1 \times 10^{-10}\ \text{cm}^3\ \text{sec}^{-1(18)}$$

$$\gamma_2 = (2{\cdot}5 \pm 0{\cdot}4) \times 10^{-11}\ \text{cm}^3\ \text{sec}^{-1(16)}$$

$$\gamma_2 = (1{\cdot}8 \pm 0{\cdot}2) \times 10^{-12}\ \text{cm}^3\ \text{sec}^{-1(17)}.$$

From ionospheric observations, values between 10^{-9} cm^3 sec^{-1} and 10^{-12} cm^3 sec^{-1} have been used to explain recombination and ionic composition; Hertzberg(19), $\gamma = 10^{-9}$ cm^3 sec^{-1}; Danilov(20), $\gamma = 10^{-10}$ cm^3 sec^{-1}; Norton, Van Zandt and Denison(3), $\gamma_2 = 5 \times 10^{-11}$ cm^3 sec^{-1}; Bates and Nicolet(21), $\gamma = 10^{-12}$ cm^3 sec^{-1}.

Langstroth and Hasted(17) have measured, for reaction (1), $\gamma_1 = (4{\cdot}7 \pm 0{\cdot}5) \times 10^{-12}$ cm^3 sec^{-1}. But before this recent experimental determination a high value of the order of 10^{-8} cm^3 sec^{-1} was given by Potter(22) and a rate coefficient of the order of 10^{-10} cm^3 sec^{-1} has been used in the study of the ionosphere by Krassovsky(23). The recent experimental analysis of Talrose, Markin and Larin(24) seems, however, to agree with a lower rate coefficient, i.e. $\gamma_1 \leqslant 6{\cdot}75 \times 10^{-12}$ cm^3 sec^{-1}. Various values have been used in the analysis of the ionospheric observations such as 10^{-9} cm^3 sec^{-1} by Hertzberg(19), 10^{-10} cm^3 sec^{-1} by Danilov(25) 1×10^{-12} cm^3 sec^{-1} by Norton, Van Zandt and Denison(3) and of the order of 10^{-13} cm^3 sec^{-1} by Bates and Nicolet(21).

Several reactions involving O_2^+ lead to NO^+, and particularly,

$$(\gamma_6);\ O_2^+(^2\Pi) + N(^4S) \rightarrow NO^+(^1\Sigma) + O(^3P) + 4{\cdot}22\ \text{eV} \tag{6}$$

$$(\gamma_7);\ O_2^+(^2\Pi) + N_2(^1\Sigma) \rightarrow NO^+(^1\Sigma) + NO(^2\Pi) + 0{\cdot}87\ \text{eV}. \tag{7}$$

This last reaction, according to Fite *et al.*(18), is very slow compared with the charge transfer process or ion-atom interchange reaction $O_2^+ + NO \rightarrow O_2 + NO^+$. However, in the atmosphere, since $n(N_2) \gg n(NO)$, (7) cannot be neglected even if the rate coefficient of the transfer process with NO is large. Reaction (6) cannot be rejected since its rate coefficient γ_6, may be much greater than γ_7 and also because in the 100 km region, where $n(N)$ is the most important fraction of the $n(N_2)$, its effect could modify the ratio $n^+(O_2)/n^+(NO)$.

The processes affecting N_2^+ involve charge transfer processes and ion-atom interchange reactions:

$$(\gamma_8);\ N_2^+(^2\Sigma) + O(^3P) \rightarrow O^+(^4S) + N_2(^1\Sigma) + 1{\cdot}96\ \text{eV} \tag{8}$$

$$(\gamma_9);\ N_2^+(^2\Sigma) + O_2(^3\Sigma) \rightarrow O_2^+(^2\Pi) + N_2(^1\Sigma) + 3{\cdot}50\ \text{eV} \tag{9}$$

$$(\gamma_{10});\ N_2^+(^2\Sigma) + N(^4S) \rightarrow N^+(^3P) + N_2(^1\Sigma) + 1{\cdot}03\ \text{eV} \tag{10}$$

$$(\gamma_{11});\ N^+(^3P) + NO(^2\Pi) \rightarrow N_2^+(^2\Sigma) + O(^3P) + 2{\cdot}22\ \text{eV}. \tag{11}$$

Finally, ion-atom interchange reactions in which N^+ and ON^+ are involved must be considered by taking into account that the lower state of ON^+ is the excited state $^3\Pi$ of the normal ion NO^+.

$$(\gamma_{12});\ N^+(^3P) + O_2(^3\Pi) \rightarrow ON^+(^3\Pi, NO^+) + O(^3P) + [6{\cdot}69 - E(^3\Pi)]\text{eV} \tag{12}$$

$$(\gamma_{13});\ N^+(^3P) + NO(^2\Pi) \rightarrow ON^+(^3\Pi, NO^+) + O(^3P) + [5{\cdot}30 - E(^3\Pi)]\text{eV} \tag{13}$$

$$(\gamma_{14}^{**});\ N_2^+(^2\Sigma) + O(^3P) \rightarrow ON^+(^3\Pi, NO^+) + N(^4S) + [3{\cdot}08 - E(^3\Pi)]\text{eV} \tag{14}$$

$$(\gamma_{15}^{*});\ N_2^+(^2\Sigma) + O_2(^3\Sigma) \rightarrow ON^+(^3\Pi, NO^+) + NO(^2\Pi) + [4{\cdot}47 - E(^3\Pi)]\text{eV}. \tag{15}$$

Reactions which may occur in the ionosphere require that the excitation energy $E(^3\Pi)$ is less than the energy balance. Thus, reaction (14) must be rejected since $E(^3\Pi)$ is more than 3 eV, for example $E(^3\Pi) = 4{\cdot}6$ eV(26). However, Norton, Van Zandt and Denison(3) have considered reaction (14) as very important in the ionosphere since they have adopted for the rate coefficient $\gamma_{14} = 2 \times 10^{-11}$ cm^3 sec^{-1}, i.e. more than the value of γ_1 for which they take 1×10^{-12} cm^3 sec^{-1}. This is based on the erroneous assumption that reaction (14) does not involve an excited electronic level of NO^+. It should be pointed out that the charge transfer ($N^+ + NO \rightarrow NO^+ + N$) is equivalent in the ion produced to reaction (13), but is different from reaction (11).

The reaction energies derived in (1) to (15) correspond to the following dissociation and ionization potentials.

Dissociation of ionized molecules:

O_2^+, 6·66 eV N_2^+, 8·73 eV NO^+, 10·88 eV.

Dissociation of neutral molecules:

O_2, 5·12 eV N_2, 9·76 eV NO, 6·51 eV.

Ionization of neutral molecules:

O_2, 12·08 eV N_2, 15·58 eV NO, 9·25 eV.

Ionization of neutral atoms:

O, 13·62 eV N, 14·55 eV H, 13·60 eV.

3. PHOTOIONIZATION PROCESSES

Reactions (1) to (13) must be used with the photo-ionization and recombination rates to write equations for electron and ion concentrations. The following ionization processes are considered:

$$I(N_2);\ N_2 + h\nu(\lambda < 796\ \text{Å}) \rightarrow N_2^+ + e \tag{16}$$

$$I_2(N);\ N_2 + h\nu(\lambda < 510\ \text{Å}) \rightarrow N + N^+ + e \tag{17}$$

$$I(N);\ N + h\nu(\lambda < 852\ \text{Å}) \rightarrow N^+ + e \tag{18}$$

$$I(O);\ O + h\nu(\lambda < 910\ \text{Å}) \rightarrow O^+ + e \tag{19}$$

$$I(O_2);\ O_2 + h\nu(\lambda < 1026\ \text{Å}) \rightarrow O_2^+ + e. \tag{20}$$

Photoionization of NO is essentially due to Lyman-α radiation at 1216 Å:

$$I(NO);\ NO + h\nu(\lambda = 1216\ \text{Å}) \rightarrow NO^+ + e \tag{21}$$

Absorption cross-sections and atmospheric densities are known with sufficient precision as far as the order of magnitude is concerned. Consequently it is possible to state that the following ionization processes occur:

(i) *D-region*

(a) Ionization of nitric oxide by Lyman-α, since O_2, N_2 and O cannot be photoionized by λ 1216·7 Å. Other constituents such as Na ($\lambda < 2412$ Å), Ca ($\lambda < 2071$ Å), CH_3 ($\lambda < 1260$ Å), C ($\lambda < 1100$ Å) can be photoionized by radiations which are unable to ionize O_2.

(b) Ionization by X-rays of $\lambda < 10$ Å, i.e. with absorption cross-sections less than 10^{-19} cm^2. It is known from rocket and satellite measurements that the Lyman-α flux is between 3 and 6 ergs cm^{-2} sec^{-1} while the X-ray flux is extremely variable with solar conditions. From 2–8 Å the minimum-to-maximum variation is a factor of several hundred (see a recent review by Friedman(27)).

(c) Ionization by cosmic rays which is effective in the lower *D*-region where Lyman-α cannot penetrate and where X-rays of $\lambda < 2$ Å are not important particularly during solar quiet conditions.

An exact analysis of the ionization problem in the *D*-region requires the determination of the separate effects of the three ionizing sources. In fact, it is necessary to compare the ionizing effect of the stable sources Lyman-α and cosmic rays compared with the extremely varying source represented by X-rays. Such an analysis has been made by Nicolet and Aikin(28) who considered various X-ray fluxes according to data obtained by the Naval Research Laboratory over an interval of several years with Lyman-α and cosmic ray ionization processes introduced by Nicolet(29,30).

The ionization rate coefficient of cosmic rays is between (Φ being the geomagnetic latitude)

$$I(\Phi \geq 0°) \geq 10^{-18}\ \text{sec}^{-1} \text{ and } I(\Phi \leq 50°) \leq 10^{-17}\ \text{sec}^{-1},$$

i.e. with the following values: $\Phi = 0°$, $1{\cdot}25 \times 10^{-18}$ sec^{-1}, $\Phi = 30°$, 2×10^{-18} sec^{-1}, $\Phi = 40°$, $4{\cdot}5 \times 10^{-18}$ sec^{-1}, $\Phi = 50°$, 1×10^{-17} sec^{-1} and $\Phi = 60°$, $1{\cdot}25 \times 10^{-17}$ sec^{-1}.

It is clear that X-rays of $\lambda \leq 2$ Å emitted during completely quiet conditions cannot lead to an ionization rate coefficient of the order of 10^{-18} sec^{-1}. On the other hand, since the ionization rate coefficient of nitric oxide by Lyman-α reaches values of the order of

$$I(NO) = 5 \times 10^{-7}\ \text{sec}^{-1},$$

a small ratio $n(NO)/n(O_2) = 10^{-10}$ leads to an electron production of the same order as the X-ray production under quiet solar conditions. Thus, disturbed solar conditions, and particularly solar flare conditions, produce a *D*-region due to X-ray radiation.

(ii) *E-region*

- (a) Ionization of molecular oxygen by ultraviolet radiation of $\lambda > 910$ Å, particularly by monochromatic radiations such as Lyman-β at 1025 Å, i.e. with absorption cross-sections between 10^{-19} cm^{-2} and 10^{-18} cm^{-2}. In addition, ionization of atomic oxygen by radiation of $\lambda < 910$ Å and, particularly, by the chromospheric Lyman continuum which can penetrate into the *E*-layer via the windows of molecular nitrogen absorption. Variation with the solar cycle of these ultraviolet radiations should be less than a factor of two.
- (b) Ionization by X-rays of $\lambda > 10$ Å and particularly by radiation in the spectral range $30 < \lambda < 100$ Å. The minimum-to-maximum solar cycle variation is approximately sevenfold(27).
- (c) Ionization of meteor atoms with low ionization potentials, introduced by Nicolet(31), to explain nocturnal conditions in the *E*-layer, and recently observed by Istomin(32).

An exact analysis of the ionization production problem in the *E*-region still requires the determination of the separate effects of the three ionizing sources. The stable source represented by ultraviolet radiations will have its maximum ionization effect under quiet solar conditions and, particularly, during the minimum of the solar cycle. X-ray action will vary with solar activity and will become predominant during disturbed solar conditions.

Considering that the ionization rate coefficient of O_2 at zero optical depth is not less than 10^{-8} sec^{-1}, it is clear that an X-ray flux varying from 0·15 to 1 erg cm^{-2} sec^{-1} for an average wavelength of 50 Å leads to an electron production from less than to greater than the ultraviolet production of O_2^+. To be consistent with solar data the ratio of electron production by ultraviolet radiations (O_2^+, O^+) and by X-rays (N_2^+, O_2^+, O^+) must decrease with increasing solar activity, but at no time may one ionization process be neglected in comparison with the other. In any case, the X-ray action must explain the behavior of the *E*-layer during the entire solar cycle.

(iii) *F-region*

- (a) Ionization of molecular nitrogen for $\lambda < 796$ Å with absorption cross-section greater than 10^{-17} cm^2.
- (b) Ionization of atomic oxygen for $\lambda < 796$ Å subject to the absorption of molecular nitrogen.
- (c) Ionization of atomic oxygen for $\lambda < 800$ Å with different absorption cross-sections for its different ionization potentials at 910 Å, 732 Å and 665 Å.

An exact analysis of the ionization problem in the *F*-region requires a simultaneous knowledge of the energy of solar emissions and of the absorption cross-sections of O, N_2 and O_2. In particular, the penetration of monochromatic solar radiations between the *E*- and *F1*-peaks must be known in order to determine the exact behavior of the electron production.

Considering that variations of solar activity will affect chromospheric and coronal lines differently, it is difficult to predict the exact height-distribution of electron production; for example, the variation of line intensity in the spectrum should be more important for the shortest wavelengths than for the Lyman continuum. However, it appears that N_2 and O ionizations will be subject to almost the same variations, and that the minimum-to-maximum variation during a solar cycle should not be greater than fourfold.

4. ELECTRON RECOMBINATION

The various processes (1) to (15) represent the most important ionospheric reactions in which nitrogen and oxygen positive ions are involved. The processes (16) to (21) correspond to photoionization of these constituents. It should be kept in mind that similar ionization processes produce metallic ions and also light ions such as He^+ and H^+. Consequently, the first recombination process to be considered is radiative recombination, such as X^+ (or XY^+) $+ e \rightarrow X$(or XY) $+ h\nu$. Since the recombination coefficient is always between 1×10^{-12} and 5×10^{-12} cm^3 sec^{-1} in the ionosphere(33), radiative recombination is neglected compared with other processes affecting ions. Three-body electronic or ionic recombination processes are also neglected since they cannot play a role in the normal ionosphere.

The essential recombination process in the ionosphere is Bates' process of neutralization due to the dissociation of a molecular ion as follows:

$$XY^+ + e \rightleftharpoons XY^* \rightarrow X^* + Y^*$$

(the * indicating possible excitation). Dissociative recombination occurs(33) as "a result of a radiationless transition to some state of the molecule in which the constituents move apart and gain kinetic energy under the action of their mutual repulsion so that the neutralization is rendered permanent by virtue of the Franck-Condon principle". It is clear from theoretical analysis that it is practically impossible to predict the temperature variation of the dissociative recombination coefficient, α. Furthermore, since the dissociation depends on the presence of a repulsive curve the absolute values of α should be different for different molecules. In other words, if values of α between 10^{-6} and 10^{-9} cm^3 sec^{-1} and variations with temperatures such as $T^{-1\pm0\cdot5}$ are assumed, they do not contradict theoretical considerations. The problem is quite complicated since there is no simple law establishing the variation of the repulsive curves of molecules. Consequently, the absolute value of α and its dependence on T must be found experimentally.

The principal dissociative recombination processes which occur in the ionosphere are:

$$\alpha(O_2);\ O_2^+ + e \rightarrow O + O \tag{22}$$

$$\alpha(NO);\ NO^+ + e \rightarrow N + O \tag{23}$$

$$\alpha(N_2);\ N_2^+ + e \rightarrow N + N. \tag{24}$$

Various experimental determinations of the recombination coefficients of these three ions exist, but it is difficult to adopt a correct value for ionospheric purposes. The determinations of $\alpha(N_2)$ at room temperature, after 1958, give 4×10^{-7} cm^3 sec^{-1}(34) and $(5\cdot9 \pm 1) \times 10^{-7}$ cm^3 sec^{-1}(35), corrected more recently to 3×10^{-7} cm^3 sec^{-1}. At high temperatures, there is an indication given by Sayers(36) for 3200°K, $\alpha(N_2) = 1\cdot1 \times 10^{-7}$ cm^3 sec^{-1}, and by Mentzoni, Montgomery and Row(37) for 725°K, $\alpha(N_2) = 6\cdot1 \times 10^{-8}$ cm^3 sec^{-1}. Consequently, $\alpha(N_2)$ is not known from laboratory measurements with sufficient precision for ionospheric purposes. However, a conclusion should be that $\alpha(N_2) > 10^{-7}$ cm^3 sec^{-1} for the lower ionosphere, and no exact value can be obtained for the upper ionosphere since the temperature variation is not known.

The recent determination of $\alpha(O_2)$ by Kasner, Rogers and Biondi(35) leading to $3{\cdot}8 \pm 1 \times 10^{-7}$ cm^3 sec^{-1} has been corrected to $1{\cdot}7 \times 10^{-7}$ cm^3 sec^{-1} (private communication) indicating that there seems to be no important difference between $\alpha(O_2)$ and $\alpha(N_2)$ at room temperature. At high temperatures the value obtained by Sayers(36), $\alpha(O_2) = 4 \times 10^{-8}$ cm^3 sec^{-1} at 2500°K, seems to indicate a rapid decrease of $\alpha(O_2)$ with temperature.

Laboratory data on α(NO) follow a pattern similar to those for $\alpha(N_2)$ and $\alpha(O_2)$. Extremely high values such as $\alpha(\mathrm{NO}) = 1{\cdot}3 \times 10^{-6}$ were recently obtained by Gunton and Inn(38), as were obtained in the 1950's (before 1958) for N_2, and values between 4×10^{-7} and 2×10^{-6} cm^3 sec^{-1} by Doering and Mahan(39). For a high temperature of about 5000°K, Lin(40) gave $\alpha(\mathrm{NO}) = 10^{-9}$ cm^3 sec^{-1}. Syverson *et al.*(41) published a value of $\alpha(\mathrm{NO}) = 1{\cdot}3 \times 10^{-7}$ cm^3 sec^{-1} at 3000°K. Thus, the temperature dependence of the coefficient is unknown.

In such circumstances it is clear that it is not possible to argue for or against any value adopted for ionospheric conditions. This points to the complexity of the determination of an ionospheric recombination coefficient depending on the recombination of several ions. Nicolet and Aikin(28) adopted $\alpha(N_2) = 5 \times 10^{-7}$ cm^3 sec^{-1}, $\alpha(O_2) = 3 \times 10^{-8}$ cm^3 sec^{-1} and $\alpha(\mathrm{NO}) = 3 \times 10^{-9}$ cm^3 sec^{-1} for their *D*-region analysis to show how ionization is affected when various constituents are involved. However, while extreme values for N_2 and NO still remain a possibility, any value of the order of 10^{-7} cm^3 sec^{-1} would not change the situation since ionic recombination and negative ions are involved.

On the other hand, Whitten and Popoff(42) have attempted to interpret the behavior of the *D*-region during ionospheric disturbances by an ionospheric coefficient between 4×10^{-7} cm^3 sec^{-1} and 4×10^{-8} cm^3 sec^{-1}. However, they claimed(43) that the *D*-region ionization can be interpreted, even during quiescent solar conditions, by X-ray radiations. Such an evaluation of the ionospheric behavior in the *D*-region indicates that an uncertainty of a factor of ten in the recombination coefficient still remains a possibility when X-ray energies are not properly related to solar conditions. Thus, any value of α from 10^{-7} to 10^{-8} cm^3 sec^{-1} used for *D*-region conditions cannot be contradicted. In fact Ivanov-Kholodny(2) adopted $\alpha = 3 \times 10^{-7} \sqrt{300/T}$ cm^3 sec^{-1} for all recombination coefficients. Norton *et al.*(3) have adopted different values: $\alpha(N_2) = 4 \times 10^{-7}(300/T)$ cm^3 sec^{-1}, $\alpha(O_2) = 2 \times 10^{-7}(300/T)$ cm^3 sec^{-1} and $\alpha(\mathrm{NO}) = 6{\cdot}7 \times 10^{-8}(300/T)$ cm^3 sec^{-1}, i.e. a variation of a factor of 6 between $\alpha(N_2)$ and α(NO). The values adopted by Ivanov-Kholodny and Norton *et al.*, demonstrate that one may estimate the absolute value of a recombination and its variation with temperature. Obviously a temperature dependence is introduced in order to follow ionospheric observations, but a coefficient varying with $T^{-1\pm0{\cdot}5}$ leads to very different values in the *F*-layer.

An analysis of ionospheric observations, such as diurnal variations or solar eclipse measurements, lead to different conclusions with recombination coefficients as low as 10^{-8} cm^3 sec^{-1} and greater than 10^{-7} cm^3 sec^{-1}(44). However, it is clear from eclipse determinations that a high value for the ionospheric recombination coefficient must be taken since there is solar emission during totality.

The night-time conditions should give a value of the recombination coefficient in the *E*-and *F1*-regions. If values of the order of 2×10^{-8}cm^3 sec^{-1}, such as reported by Titheridge(45), are accepted for night-time conditions, they should represent the recombination coefficient of the predominant ion. However, it is not yet clear what the exact vertical distribution of electrons is in the night-time *E*- and *F1*-layers. If there is a peak in the *E*-layer due to meteor ions, the analysis of the normal recombination is perturbed. If the electron concentration at ionosphere sunset is $n_{e,o}$ its value $(n_e)_t$ after t sec is given by

$$(n_e)_t = \frac{1}{\alpha t + 1/n_{e,o}}.$$

Thus, after 4×10^4 sec, the following values are obtained:

$\alpha(\text{cm}^3\ \text{sec}^{-1}) =$	$2{\cdot}5 \times 10^{-7}$	$2{\cdot}5 \times 10^{-8}$	$2{\cdot}5 \times 10^{-9}$	$2{\cdot}5 \times 10^{-10}$
$(n_e)_t(\text{cm}^{-3}) \leq$	10^2	10^3	10^4	10^5
$n_{e,0}(\text{cm}^{-3}) >$	10^3	10^4	10^5	10^6

Electron concentrations of the order of 10^3 cm^{-3} below the *F2*-region require an electron recombination coefficient of the order of $2{\cdot}5 \times 10^{-8}$ cm^3 sec^{-1} for a predominant ion such as NO^+, or the presence of meteor ions with radiative recombination coefficients. A value of α reaching 10^{-7} cm^3 sec^{-1} cannot result in more than $2{\cdot}5 \times 10^2$ electrons at the end of the night. Nevertheless, types of E_S ionization could modify the analysis since ion behavior is different according to the nature of the ions. For example, meteor ions and nitric oxide are not subject to resonance charge transfer as is the case for O_2^+, O^+ and N_2^+, and their redistributions in the presence of the Earth's magnetic field are different. There is also the problem of the recombination coefficient changing with time due to its dependence on electronic and ionic temperatures. In any event, it must be remembered that the electron-ion collision frequency decreases with temperature ($\propto T^{-3/2}$) and that the normal tendency of the temperature dependence of α_D, therefore, should be, in a complicated way, to decrease with increasing temperatures.

5. NEGATIVE IONS

The reactions in which negative ions are involved are important in the *D*-region and must be added to the preceding reactions. The mutual neutralization reaction between positive and negative molecular ions such as

$$\alpha_i;\ XY^+ + O_2^- \rightarrow (X + Y) + O_2 \tag{25}$$

will add to the dissociative recombination $\alpha(XY)$ an additional term $\alpha_i\lambda$ where λ is the ratio of negative ion and electron concentrations for equilibrium conditions. In the same way

$$\alpha_i;\ O^+ + O^- \rightarrow O + O \tag{26}$$

could be considered in a certain ionospheric region. The rate coefficients of reactions such as (25) and (26) are not accurately known(46); values between 10^{-7} and 10^{-8} cm^3 sec^{-1} are possible.

The introduction of negative ions in the *D*-region certainly depends on the three-body attachment

$$a(O_2);\ O_2 + O_2 + e \rightarrow O_2^- + O_2 \tag{27}$$

for which Chanin, Phelps and Biondi(47) have obtained an experimental value of the order of $2{\cdot}3 \times 10^{-30}$ cm^6 sec^{-1} for low atmospheric temperatures. For atomic oxygen, radiative attachment is an essential process

$$a(O);\ O + e \rightarrow O^- + h\nu \tag{28}$$

for which an attachment coefficient of the order of $1{\cdot}3 \times 10^{-15}$ cm^3 sec^{-1} has been deduced from the photodetachment cross-section measured by Branscomb, Burch, Smith and Geltman(48).

For such negative ions, photodetachment by solar radiation leads to a photodetachment

$$d(O^-) = 1{\cdot}4 \text{ sec}^{-1} \tag{29}$$

using experimental data obtained by Branscomb *et al.*(48) while $d(O_2^-)$ is about 10 times smaller than (29). Photodetachment is the principal loss process for negative ions in a sunlit atmosphere while mutual neutralization is important in the night-time *D*-region. It should be noted that ions such as O^+ do not exist at low altitudes due to ion-atom interchange reactions. Furthermore, O_2^+ is involved in an ion-atom interchange reaction leading to NO^+. Thus, the positive ions in (25) must be the molecular ions O_2^+ and NO^+.

In the lower night-time *D*-region, atomic oxygen is excluded from collisional detachment of a negative ion because it disappears via ozone formation. Negative ions such as OH^-, O_3^- and NO_2^-, for which higher affinities exist, depend on the behavior of O_2^- and may be considered as playing a role during twilight conditions. In other words, their concentrations are related to $n(O_2^-)$ for night-time conditions through reactions which generally involve atoms. For example, $n(O_3^-)/n(O_2^-)$ depends on $n(O)$, $n(NO_2^-)/n(O_2^-)$ depends on $n(N)$; i.e on atoms which are not important in the lower *D*-region after sunset.

Charge transfer processes should be considered. For example, the OH ion under the same conditions should increase since a charge transfer such as $OH + O_2^- \rightarrow OH^- + O_2$ will not be compensated by collisional detachment with atomic hydrogen, H, which is unimportant where OH can play a role. Finally, all reactions leading to NO_2^-, an ion having a high affinity (greater than 3·8 eV according to Curran(49)) should be studied.

For other conditions, the processes of associative detachment discussed by Dalgarno(46), i.e.

$$O^- + O \rightarrow O_2 + e \tag{30}$$

$$O_2^- + O \rightarrow O_3 + e \tag{31}$$

are certainly the most important processes for collisional detachment. Thus, even for night-time conditions, negative ions are important only in the *D*-region, and it is difficult to find adequate processes to introduce negative ions in the *E*-layer.

6. ANALYSIS OF IONOSPHERIC REACTIONS

(1) *General conditions*

All processes (1) to (24) (after neglecting the effect of negative ions) must be considered in order to determine the essential reactions in the ionosphere. The scheme of Fig. 1 gives a general idea of the relationships between the various processes. From this, it is clear that only NO^+ can be considered as disappearing by dissociative recombination alone, O_2^+ and N_2^+ concentrations are affected by ion-atom interchange reactions (γ_6 and γ_7) and by charge transfer processes (γ_8 and γ_9) respectively. O^+ is transformed into molecular ions by ion-atom interchange reactions (γ_1–γ_4). Its transformation into NO^+ is due to reactions with N_2 and NO (γ_1 and γ_3) and into O_2^+ by O_2 and NO (γ_2 and γ_4). However, O^+ production is increased by the charge transfer process between atomic oxygen and molecular nitrogen ions (γ_8). The ratio $n^+(O_2)/n^+(NO)$ is not independent of reactions leading to O_2^+ or NO^+ since O_2^+ may transform into NO^+ by ion-interchange reactions (γ_7 and γ_6).

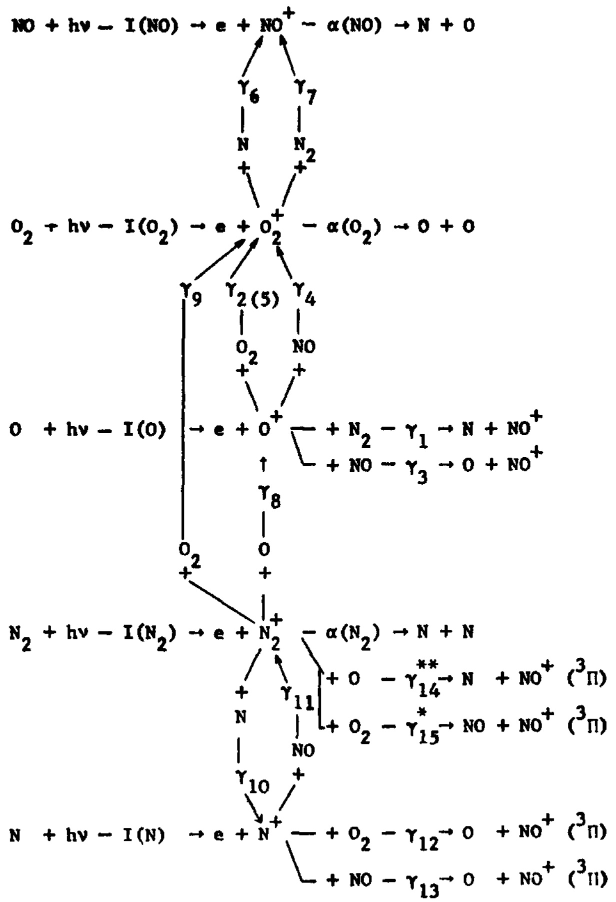

FIG. 1. IONOSPHERIC REACTIONS. PHOTOIONIZATION WITH RATE COEFFICIENT I, DISSOCIATIVE RECOMBINATION WITH COEFFICIENT α, CHARGE TRANSFER OR ION-ATOM INTERCHANGE WITH COEFFICIENT γ.

(2) *Equilibrium conditions*

In order to determine the relative importance of reaction (1) to (24), ionization equations are first considered for steady state conditions. They may be written as follows

$$n^+(N_2) = \frac{n(N_2)I(N_2) + n^+(N)\gamma_{11}n(NO)}{\alpha(N_2)n_e + \gamma_8 n(O) + \gamma_9 n(O_2) + \gamma_{10}n(N)} \tag{32}$$

$$n^+(N) = \frac{n(N_2)I_2(N) + n(N)[I(N) + \gamma_{10}n^+(N_2)]}{\gamma_{12}n(O_2) + [\gamma_{11} + \gamma_{13}]n(NO)} \tag{33}$$

$$n^+(O) = \frac{n(O)[I(O) + \gamma_8\, n^+(N_2)]}{\gamma_1 n(N_2) + \gamma_2 n(O_2) + [\gamma_3 + \gamma_4]n(NO)} \tag{34}$$

$$n^+(O_2) = \frac{n(O_2)[I(O_2) + \gamma_2 n^+(O) + \gamma_9 n^+(N_2)] + n(NO)\gamma_4 n^+(O)}{\alpha(O_2)n_e + \gamma_6 n(N) + \gamma_7 n(N_2)} \tag{35}$$

$$\begin{aligned} n^+(NO) = \frac{1}{\alpha(NO)n_e} \Big\{ & n^+(O)[\gamma_1 n(N_2) + \gamma_3 n(NO)] + n^+(O_2) \\ & \times [\gamma_6 n(N) + \gamma_7 n(N_2)] + n^+(N)[\gamma_{12}n(O_2) + \gamma_{13}n(NO)] + n(NO)I(NO) \Big\}. \end{aligned} \tag{36}$$

In the denominator of (32) the process $N_2^+ + NO \rightarrow NO^+ + N_2$ has not been introduced, since the concentration of nitric oxide is only a fraction of that of molecular oxygen. According to Nicolet's formula(50), adapted to recent rate coefficient,

$$n(NO) = n(O_2) \times 10^{-1}\, e^{-3000/T} \tag{37}$$

which shows that $n(NO)$ is always a small fraction of $n(O_2)$. With diffusion conditions for nitric oxide, $n(NO)$ and $n(O_2)$ decrease with height at almost at the same rate since $M(NO) = 30$ and $M(O_2) = 32$, and the ratio $n(NO)/n(O_2)$ almost corresponds to the ratio fixed by photo-equilibrium conditions at the lower boundary of the diffusion region.

On the other hand, reactions (14) and (15), which would lead directly to NO^+, are not considered since (8) and (9) are more effective processes. However, a special remark must be made here on the problem of nitric oxide, since Danilov claimed that the relation (37) cannot be accepted. His arguments are based on the assumption that molecular oxygen is strongly dissociated at 150–160 km altitude(51). In fact, he assumed the following equilibrium:

$$\alpha_D n^+(O_2) n_e = \gamma n^+(O) n(O)$$

where the rate coefficient α_D of the dissociative recombination is 10^{-6} cm^3 sec^{-1}, while the rate coefficient γ for a radiative association of O_2^+ is about 5×10^{-11} cm^3 sec^{-1}. Such a value is much too great for a radiative association(52); by a factor of 10^5–10^6. With 5×10^{-11} cm^3 sec^{-1}, we obtain

$$-\frac{1}{n^+(O)}\frac{dn^+(O)}{dt} \geq 5 \times 10^{-11}\, n(O)$$

and we find that, for $n(O) \geq 10^7$ cm^{-3}, a time shorter than 10^4 sec would reduce the sunset concentration to less than 1 per cent. For example, no night-time ionosphere at 300–350 km, where $n(O) = 5 \times 10^8$ cm^3, can exist after a few hundred seconds. In order to maintain the observed ion concentration, a night-time production of more than 1000 ions cm^{-3} sec^{-1} should be required at all latitudes. The same remark must be applied to the dissociation of nitrogen. Danilov(52) introduces also the reaction

$$N + N \rightarrow N_2 + h\nu$$

with a rate coefficient of the order of 3×10^{-11} cm^3 sec^{-1} which is too great by a factor of several hundred thousands.

In fact, the problem must be considered as follows. The extent to which molecular oxygen is dissociated depends on the importance of the loss processes (2), in addition to normal photodissociation $J(O_2)$ compared with vertical transport, w, by diffusion. A continuity equation such as

$$\frac{dn(O_2)}{dt} = \frac{d[n(O_2)w]}{dz} - n(O_2)[J(O_2) + \gamma_2 n^+(O)],$$

since $J(O_2) > 10^{-6}$ sec^{-1} with the use of $\gamma_2 \leq 10^{-12}$ cm^3 sec^{-1}, shows that the diffusion distribution of molecular oxygen represents, in a first approximation, the vertical distribution of that molecule. The disappearance of molecular oxygen in the *F2*-region as claimed by Danilov should lead to such a strong departure from diffusive equilibrium distribution, that an upward vertical flow of O_2 molecules is immediately supported by diffusion. It can easily reach more than 10^{11} molecules cm^{-2} sec^{-1} at 150 km and remains greater than 10^{10} molecules cm^{-2} sec^{-1} at 250 km. Thus, there is no difficulty in relating the dissociation of nitrogen to the vertical distribution of molecular oxygen.

In fact, atomic nitrogen reacts with O_2 according to the process

$$\mathrm{N} + \mathrm{O_2} \rightarrow \mathrm{NO} + \mathrm{O}$$

for which the rate coefficient b_1 can be written

$$b_1 = 1{\cdot}5 \times 10^{-13} T^{1/2} e^{-3000/T}$$

showing the strong effect of the temperature. An important loss process for atomic nitrogen occurs in the $F1$-region where the temperature is high and where there is still a sufficient number of O_2 molecules. Furthermore, nitric oxide reacts easily with N according to

$$\mathrm{N} + \mathrm{NO} \rightarrow \mathrm{N_2} + \mathrm{O}$$

for which a rate coefficient b_2 may be written

$$b_2 = 1{\cdot}5 \times 10^{-12} T^{1/2},$$

with practically no activation energy. In chemical equilibrium, (37) represents, therefore, the exact conditions. Thus, the mechanism of atomic nitrogen recombination and that of the formation of O_2^+ ions proposed by Danilov cannot be accepted since they are based on the assumption that radiative associations have rate coefficients of the order of 10^{-11} cm^3 sec^{-1}.

It follows from the preceding remarks that an adequate approximation for (32) to (36) is introduced by neglecting reactions (3), (4), (11) and (13) in that $\gamma n(\mathrm{NO}) \ll \gamma n(\mathrm{O_2})$ or $\gamma n(\mathrm{N_2})$.

In all the ionization equations (32) to (36) there is competition between reactions depending on the neutral constituent concentrations. A simple way to investigate the various effects is to introduce numerical factors having all possible values between 0 and 1. They are: (a) for loss of atomic oxygen ions

$$A = \frac{\gamma_2 n(\mathrm{O_2})}{\gamma_1 n(\mathrm{N_2}) + \gamma_2 n(\mathrm{O_2})}; \qquad 1 - A = \frac{\gamma_1 n(\mathrm{N_2})}{\gamma_1 n(\mathrm{N_2}) + \gamma_2 n(\mathrm{O_2})}. \tag{38}$$

(b) for production of atomic oxygen ions,

$$B = \frac{\gamma_8 n(\mathrm{O})}{\gamma_8 n(\mathrm{O}) + \gamma_9 n(\mathrm{O_2})}; \qquad 1 - B = \frac{\gamma_9 n(\mathrm{O_2})}{\gamma_8 n(\mathrm{O}) + \gamma_9 n(\mathrm{O_2})}. \tag{39}$$

(c) for loss of molecular nitrogen ions,

$$C = \frac{\alpha(\mathrm{N_2}) n_e}{\alpha(\mathrm{N_2}) n_e + \gamma_8 n(\mathrm{O}) + \gamma_9 n(\mathrm{O_2})}; \qquad 1 - C = \frac{\gamma_8 n(\mathrm{O_2}) + \gamma_9 n(\mathrm{O_2})}{\alpha(\mathrm{N_2}) n_e + \gamma_8 n(\mathrm{O_2}) + \gamma_9 n(\mathrm{O_2})}. \tag{40}$$

(d) for loss of molecular oxygen ions,

$$D = \frac{\alpha(\mathrm{O_2}) n_e}{\alpha(\mathrm{O_2}) n_e + \gamma_6 n(\mathrm{N}) + \gamma_7 n(\mathrm{N_2})}; \qquad 1 - D = \frac{\gamma_6 n(\mathrm{N}) + \gamma_7 n(\mathrm{N_2})}{\alpha(\mathrm{O_2}) n_e + \gamma_6 n(\mathrm{N}) + \gamma_7 n(\mathrm{N_2})}. \tag{41}$$

(3) *Molecular nitrogen ion*

The ion N_2^+ is a minor constituent in the ionosphere(54–56), even if its production by ultraviolet radiation $n(\mathrm{N_2})\mathrm{I}(\mathrm{N_2}) \equiv q(\mathrm{N_2})$ is important. Equation (32) becomes, after making the approximations justified before,

$$n^+(\mathrm{N_2}) = \frac{q(\mathrm{N_2})}{\alpha(\mathrm{N_2}) n_e + \gamma_8 n(\mathrm{O}) + \gamma_9 n(\mathrm{O_2})} \tag{42}$$

showing that various loss processes dominate depending on the latitude involved. It must be pointed out here that Danilov(57) has introduced a concept which cannot be accepted. Instead of using the charge transfer or ion-atom interchange (10)

$$N_2^+ + N \rightarrow N^+ + N_2 + 1{\cdot}03 \text{ eV}$$

he considered the opposite endothermic reaction

$$N^+ + N_2 \rightarrow N_2^+ + N - 1{\cdot}03 \text{ eV}$$

with a rate coefficient of the order of 10^{-11} cm^3 sec^{-1}.

It is not permissible to ignore an exothermic reaction when the opposite endothermic reaction is used, even if the ratio of the N_2^+ and N^+ concentrations that Danilov(57) obtained agrees with the observed values. The reasoning is incorrect and the numerical values used are wrong. The relative concentration of N_2^+ in the *E*-layer is very small, but its bands are observed in the twilight airglow, even though the night-time intensity is very low ($\leq 5 \times 10^6$ photons cm^{-2} sec^{-1}) during quiet magnetic conditions The twilight observations must be explained by a fluorescence effect of solar radiation on N_2^+ ions which are present in the *F2*-region. The mid-day production of N_2^+ is due to solar radiation of $\lambda < 796$ Å which are absorbed in the *F1*-region; X-rays of $\lambda < 10$ Å are absorbed in the *E*-layer; X-rays shorter than 10 Å are absorbed in the *D*-region, and cosmic rays ionize N_2 in the lower part of the *D*-region(28). There is, therefore, a production of N_2^+ ions in the whole ionosphere, i.e. where the electron concentration varies from 10^2 cm^{-3} to 10^6 cm^{-3}. In other words, the first term in the denominator of (42) corresponding to dissociative recombination is not always the most important term; N_2^+ can be transformed, before dissociative recombination by charge transfer process (8) and (9) involving O^+ and O_2^+, respectively. Thus the ionization equation (42) becomes, by using (40),

$$n^+(N_2) = \frac{Cq(N_2)}{\alpha(N_2)n_e} \tag{43a}$$

$$n^+(N_2) = \frac{(1 - C)q(N_2)}{\gamma_8 n(O) + \gamma_9 n(O_2)} \tag{43b}$$

in which $0 \leq C \leq 1$ increases with height. With electron concentrations of the order of 10^6 cm^{-3}, i.e. in the *F2*-layer, the lifetime of N_2^+ is very short since it depends on an exponential term approximately as follows

$$n^+(N_2) = n_0^+(N_2)e^{-\alpha(N_2)n_e t} + \frac{q(N_2)}{\alpha(N_2)n_e}[1 - e^{-\alpha(N_2)n_e t}] \tag{44}$$

leading to

$$\tau(N_2^+) = 1/\alpha(N_2)n_e \tag{45}$$

namely a few hundred seconds as a maximum lifetime.

Thus, photoequilibrium represents the ionization conditions for N_2^+. Nevertheless, an exact analysis of aeronomic data is difficult since a determination of the factor *C* in equation (43a) is needed. An aeronomic determination cannot lead to a precise knowledge of rate coefficients for which experimental data are still lacking. Since the theoretical analysis shows that there must be a transformation of N_2^+ into O_2^+ in the *D*-region, and into O^+ up to the *F*-region, it is shown under which conditions charge transfer processes (8) and (9) should dominate.

Let us take 5×10^{-7} cm^3 sec^{-1} as a working (maximum) value for $\alpha(N_2)$. In the *D*-region (60–80 km), $\gamma_9 n(O_2) \geq \alpha_{N_2} n_e$ when

$$\begin{aligned} n(O_2) &= 10^{15} && = 10^{14}\ \text{cm}^{-3} \\ \alpha(N_2)n_e &= 5 \times 10^{-5(*)} && = 5 \times 10^{-4}\ \text{sec}^{-1} \\ \gamma_9 &\geq 10^{-19} && \geq 10^{-17}\ \text{cm}^3\ \text{sec}^{-1}. \end{aligned}$$

Such values of γ_9, corresponding to charge transfer cross-sections less than 10^{-23} cm^2 show that there is no problem in considering the transformation of N_2^+ into O_2^+ in the *D*-region. In addition, the following charge transfer process can be adopted for argon

$$A^+ + N_2 \rightarrow N_2^+ + A$$

and thus the ionospheric conditions resulting from the ionization of the principal atmospheric constituents by cosmic rays and by X-rays lead to molecular oxygen ions.

As far as the *E*-region (100–120 km) is concerned, the same analysis for O_2 and O gives

$$\begin{aligned} n(O_2), n(O) &= 10^{12} && = 10^{11}\ \text{cm}^{-3} \\ \alpha(N_2)n_e &= 5 \times 10^{-2}\ \text{sec}^{-1} \\ \gamma_8, \gamma_9 &\geq 10^{-13} && \geq 10^{-12}\ \text{cm}^3\ \text{sec}^{-1}. \end{aligned}$$

The small amount of N_2^+ in the *E*-region cannot be justified if only dissociative recombination is involved. It can be justified if the rate coefficients γ_8 or γ_9 reach values of the order of 10^{-12} cm^3 sec^{-1}, i.e. a charge transfer cross-section of the order of 5×10^{-18} cm^2 corresponding to 1/1000 times a resonance charge transfer. Without increasing the preceding value of γ_8 in the *F*-region, a decrease with temperature of the dissociative recombination coefficient must be introduced. With, for example, $\alpha(N_2) = 5 \times 10^{-8}$ cm^3 sec^{-1}, the following conditions are obtained for the *F*-region:

Altitude	150	300	500 km
$n(O)$	$= 10^{10}$	$= 10^9$	$= 10^8$ cm^{-3}
$\alpha(N_2)n_e$	$= 10^{-2}$	$= 5 \times 10^{-2}$	$= 10^{-2}$ sec^{-1}
γ_8	$\geq 10^{-12}$	$\geq 10^{-11}$	$\geq 10^{-11}$ cm^3 sec^{-1}.

Thus, if the charge transfer process (8) has a rate coefficient of the order of 10^{-12} cm^3 sec^{-1} an additional production of atomic oxygen ions results from the general photo-ionization of molecular nitrogen. Bearing in mind that the production rate of N_2^+ is important in the *F1*-layer, it is clear that the production of O^+ should be increased as compared with its direct production by photoionization of atomic oxygen. The transformation of N_2^+ into O^+ is a process different from an ion-atom interchange reaction leading to NO^+ indicating that the role played by N_2^+ in the *E* and *F1*-layers does not correspond to that which Norton, Van Zandt and Denison(3) assumed.

From the present analysis of reactions involving N_2^+ ions, it appears that N_2^+ concentrations are not directly related to the nature of other ions but to the presence of electrons and the concentrations of neutral constituents. In addition, N_2^+ may always be considered as essentially being in photoionization equilibrium in all ionospheric layers.

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* Ionic recombination is neglected here; its effect is small at 80 km.

(4) *Atomic nitrogen ion*

Atomic nitrogen is a minor constituent(50) and its ion, N^+, exists only above the *F1*-layer, being a certain fraction of $O^+(<10\%)$ in the *F2*-layer(54). The N^+ concentration is given essentially by the following approximation of (33)

$$n^+(N) = \frac{n(N_2)I_2(N) + n(N)[I(N) + \gamma_{10}n^+(N_2)]}{\gamma_{12}n(O_2)}. \tag{46}$$

The principal loss process of N^+ occurs by ion-atom interchange reactions with O_2 which apparently is very rapid. According to laboratory measurements made by Fite *et al.*(18) a tentative value for the rate coefficient γ_{12} should be of the order of 5×10^{-10} cm^3 sec^{-1}. Even if such an experimental value is not precise, equation (46) shows that the absence of N^+ ions in the low ionosphere can be easily justified.

The first process of N^+ production is due to the dissociative photoionization of molecular nitrogen and requires the effect of solar radiation of $\lambda < 510$ Å. According to Weissler *et al.*(58), the ionization cross-section of the process

$$N_2 + h\nu(\lambda < 510\ \text{Å}) \rightarrow N^+(^3P) + N(^4S) \tag{47}$$

is of the order of 10^{-19} cm^2, i.e. about 100 times less than the ionization cross-section leading to N_2^+. Since the ratio of molecular and atomic nitrogen concentrations $n(N_2)/n(N)$ is much greater than 100 at normal ionospheric levels, the ionization rate for atomic nitrogen at $\lambda < 510$ Å is due to the dissociative photoionization of N_2. In fact, since the optical depth for $\lambda < 800$ Å depends on molecular nitrogen absorption, there is only the narrow spectral range between 850 and 800 Å, which leads to a direct photoionization of N completely independent of N_2. Thus, using (43b), (46) is written as follows

$$n^+(N) = \frac{q(N) + \gamma_{10}n\,(N)(1 - C)q(N_2)/[\gamma_8 n(O) + \gamma_9 n(O_2)]}{\gamma_{12}n(O_2)} \tag{48}$$

or, by the generally adequate approximation,

$$n^+(N) = \frac{n(N_2)I_2(N)}{\gamma_{12}n(O_2)}. \tag{49}$$

When the optical depth becomes small enough (above the *F1*-peak) the N^+ concentration after a rapid increase, should be

$$n^+(N) \propto I_2(N)/\gamma_{12} \tag{50}$$

i.e. almost proportional to the ratio of rate coefficients since the variation of $n(N_2)/n(O_2)$ increases slowly with height.

From considerations of observational data obtained by Istomin(54), it appears that $n^+(N)$ is not less than 10^4 cm^{-3} above the *F2*-peak and can be obtained from an equation such as (49). At sufficiently high altitudes, the lifetime of N^+ ions, is however, very long, since

$$\tau(N^+) = 1/\gamma_{12}n(O_2) \tag{51}$$

and (49) should only be used to determine the ion concentration for boundary conditions of the diffusive distribution above the *F2*-peak. Also note that reaction (12) does not play a major role in creating NO^+, since reaction (1) involving O^+ and N_2 is, in fact, the essential process. From the present analysis it appears that the N_2 concentration is not directly related to the presence of other ions but essentially to molecular oxygen. Thus, it can be neglected when the ionization conditions for all other ions are studied. Furthermore, the endothermic reaction $N^+ + N_2 \rightarrow N_2^+ + N$ used by Danilov(57) must be rejected since the interchange process transforming the molecular ion N_2^+ into the atomic ion N^+ is an exothermic reaction.

(5) *Atomic oxygen ions*

The principal reactions in which O^+ is involved lead to the following simplification of equation (34) for photoionization equilibrium,

$$n^+(\mathrm{O})_{\mathrm{eq}} = \frac{q(\mathrm{O}) + n^+(\mathrm{N_2})\gamma_8 n(\mathrm{O})}{\gamma_1 n(\mathrm{N_2}) + \gamma_2 n(\mathrm{O_2})}\,. \tag{52a}$$

The loss of O^+ ions by the associative process

$$O^+ + O \rightarrow O_2^+ \, h\nu$$

with a rate coefficient certainly less than 10^{-16} cm^3 sec^{-1} is, of course, ignored in the presence of ion atom interchange reactions (1) and (2). The production of O^+ ions by the endothermic reaction

$$O_2^+ + N \rightarrow NO + O^+ - 0{\cdot}15\ \mathrm{eV}$$

is not considered, since it cannot play an important role compared with other production sources.

With (39) and (43b), the steady state value (52a) becomes

$$n^+(\mathrm{O})_{\mathrm{eq}} = \frac{q(\mathrm{O}) + B(1 - C)q(N_2)}{\gamma_1 n(\mathrm{N_2}) + \gamma_2 n(\mathrm{O_2})} \tag{52b}$$

in which $O \leq B \leq 1$.

In the lower ionosphere B and C decrease to very small values while they increase with height in the *F*-region. The maximum effect for an additional production of O^+ ions should occur for $B = 1$ and $C = 0$. Such conditions are never reached but are best approached in the *F1*-layer. Thus, there is a contribution to the direct photoionization of atomic oxygen by the effect of photoionization of molecular nitrogen leading to an important production of the O^+ ion. At altitudes corresponding to the *E*-layer, ion-atom interchange reactions (1) and (2) are important enough to transform O^+ ions into NO^+ and O_2^+. If approximate ionization equilibrium can be retained for daytime conditions in the *F1*-layer according to ionospheric observations, they must be rejected for the *F2*-layer. Daytime and night-time conditions for *F1*- and *F2*-layers clearly show that the loss coefficient

$$\gamma_1 n(\mathrm{N_2}) + \gamma_2 n(\mathrm{O_2}) = \beta(z) \tag{53}$$

becomes small so that

$$n^+(\mathrm{O}) = n^+(\mathrm{O})_{t=0} e^{-\beta(z)t} + n^+(\mathrm{O}) = [1 - e^{-\beta(zt)}]. \tag{54}$$

In other words, the low electronic concentration in the *F1*-layer for night-time conditions mean that the principal loss processes (1) and (2) for atomic oxygen ions are large, and that steady state conditions can be used for daytime conditions. In the *F2*-layer, the night-time concentration of O^+ ions is such that the steady state is far from being an adequate approximation for real conditions, which depend on diffusion processes. In fact, it is well known that diffusion leads to the *F2*-peak and is active above it, so that photoequilibrium cannot be applied in that region.

From the analysis of ionospheric conditions by Danilov(57) and Ivanov-Kholodny(2), high values of γ of not less than 10^{-11} cm^3 sec^{-1} are deduced since $\beta(z)$ is at least 10^{-4} sec^{-1} and 10^{-3} sec^{-1} at 500 km and 300 km, respectively. All other results which have been obtained, however, lead to values less than 10^{-3} sec^{-1} at 300 km. For example, $\beta(300 \text{ km}) = 6{\cdot}8 \times 10^{-4}$ sec^{-1} given by Van Zandt *et al.*(59) is the largest value which is obtained for daytime conditions near sunspot maximum. A low value $\beta(300 \text{ km}) = 10^{-4}$ sec^{-1} is deduced by Ratcliffe *et al.*(60) for night-time data. A recent analysis made by Nisbet and Quinn(61) leads to even smaller values for night-time data which must correspond to low temperatures of the thermopause.

It is clear, therefore, that equilibrium conditions cannot represent real conditions if $\beta(z) = \gamma n \leq 10^{-4}$ sec^{-1}. Equations (53) and (54) show that from such observational results γ cannot reach 10^{-11} cm^3 sec^{-1}. A maximum average value should be $\gamma \leq 10^{-12}$ cm^3 sec^{-1}. Furthermore, it is necessary to know the exact ratio γ_1/γ_2 in order to distinguish between the ion-atom interchange reactions of O^+ with N_2 and O_2. It is not possible to obtain exact aeronomic conditions without knowing the ratio $\gamma_1 n(N_2)/\gamma_2 n(O_2)$. Again an apparent interpretation of ionospheric behavior may be given with an arbitrary hypothesis since very many parameters are involved for which accurate values are as yet unknown.

(6) *Molecular ions* O_2^+ *and* NO^+

Mass-spectrometric measurements(55,56,62), show that O_2^+ and NO^+ are the principal ions in the *E*-layer and that O^+ becomes important only in the *F1*-layer. Equilibrium conditions may be considered as a very good approximation to study the general behavior of molecular ions in a sunlit atmosphere, since they disappear via dissociative recombination.

Again neglecting reactions with NO, (35) and (36) are written as follows

$$n^+(NO)\{\alpha(NO)n_e\} = q(NO) + [1 - A][\gamma_1 n(N_2) + \gamma_2 n(O_2)]n^+(O) + [\gamma_6 n(N) + \gamma_7 n(N_2)]n^+(O_2) \quad (55)$$

$$n^+(O_2)\{\alpha(O_2)n_e + \gamma_6 n(N) + \gamma_7 n(N_2)\} = q(O_2) + A[\gamma_1 n(N_2) + \gamma_2 n(O_2)]n^+(O) + [1 - B][\gamma_8 n(O) + \gamma_9 n(O_2)]n^+(N_2). \quad (56)$$

It should again be made clear that we do not introduce, in the presence of the ion-atom interchange (2),

$$O^+ + O_2 \rightarrow O_2^+ + O \quad (5)$$

or the production of molecular oxygen by the radiative association

$$O^+ + O \rightarrow O_2^+ + h\nu$$

introduced by Danilov(51) since the rate coefficient he has used, i.e. 5×10^{-11} cm^3 sec^{-1}, is too great by a factor of about 10^6. Equations (55) and (56) show how $n^+(NO)$ and $n^+(O_2)$ are related to the same loss reactions of atomic oxygen ions. An exact knowledge of the factor A defined by (38) is first required. But the ratio $n^+(NO)/n^+(O_2)$ is subject to the effect of reactions (6) and (7) leading to a transformation of O_2^+ into NO^+. Equation (55) leads to

$$\frac{n^+(NO)}{n^+(O_2)} \geq \frac{\gamma_6 n(N) + \gamma_7 n(N_2)}{\alpha(NO)n_e}. \quad (57)$$

In the *E*-region, where $n_e = 10^5$ cm^{-3} and $n(N_2) = 10^{13}$ to 10^{12} cm^{-3}, a value $\gamma_7 \geq 10^{-15}$ cm^3 sec^{-1} leads to $n^+(NO) > n^+(O_2)$ if $\alpha(NO) = 10^{-7}$ to 10^{-8} cm^3 sec^{-1}. Thus, if one assumes that the cross-section $Q(O_2^+ - N_2)$ can reach 10^{-20} cm^2, there is a transformation of ions O_2^+ into NO^+ at the bottom of the *E*-layer. Such a value of γ_7 would lead to a complete transformation of all ions into NO^+ in the *D*-region, since N_2^+ can also be transformed into O_2^+ according to charge transfer process (9).

There is, therefore, an important problem to be resolved before determining the exact behavior of the *D*-region and lower *E*-layer. All mass-spectrometric observations, except perhaps during disturbed conditions, seem to show an increase of NO^+ compared with O_2^+ toward low altitudes. In addition, reaction (6) involving nitrogen atoms should be considered as a process transforming O_2^+ into NO^+ since atomic nitrogen reaches its maximum concentration in the *E*-layer(50). A high, but not impossible value of γ_6 is required. As far as the reaction $O_2^+ + NO \rightarrow NO^+ O_2$ is concerned, it should not be compared with (6) since $n(NO)$ is a very small fraction of $n(N)$ in the *E*-layer according to equation (37). In any case, the present analysis shows that the behavior of the lower ionosphere cannot be studied by ignoring the possible effect of reactions (6) and (7).

Above a certain altitude, it is clear that O^+ is more important than O_2^+ in the production of the NO^+ ion. Equation (55) leads to

$$\frac{n^+(NO)}{n^+(O)} \geq \frac{\gamma_1 n(N_2)}{\alpha(NO)n_e} \tag{58}$$

which becomes, where $n^+(O) \simeq n_e$.

$$n^+(NO) \geq \gamma_1 n(N_2)/\alpha(NO). \tag{59}$$

Equations (58) and (59) should be applied to the *F1*- and *F2*-layers, respectively; the NO^+ production essentially depends on the ion-atom interchange reaction (1).

Analysis of (56) shows that the direct production of O_2^+ ions by photoionization is an important process since all solar radiation of $\lambda < 1026$ Å is involved. But the final concentration $n^+(O_2)$ is related to the effect of its transformation into NO^+ by reactions (6) and (7). Above a certain altitude, (56) leads to

$$\frac{n^+(O_2)}{n^+(O)} \geq \frac{\gamma_2 n(N_2) + q(O_2)/n^+(O)}{\alpha(O_2)n_e} \tag{60}$$

which becomes, where $n^+(O) \simeq n_e$,

$$n^+(O_2) \geq \frac{q(O_2)}{\alpha(O_2)n^e} + \frac{\gamma_2 n(O_2)}{\alpha(O_2)}. \tag{61}$$

Equations (60) and (61) should be applied to the *F1*- and *F2*-layers, respectively; O_2^+ production depends on the ion-atom interchange reaction (2) together with direct photoionization.

The general ionization equations (55) and (56) can be written, using equilibrium conditions (43b) and (52b),

$$n^+(NO)\{\alpha(NO)n_e\} = q(NO) + [1 - A]q(O) + [1 - C][B - AB]q(N_2) + n^+(O_2)[\gamma_6 n(N) + \gamma_7 n(N_2)] \tag{62}$$

and

$$n^+(O_2)\{\alpha(O_2)n_e\} = q(O_2) + Aq(O) + [1 - C][1 - (B - AB)]q(N_2) - n^+(O_2)[\gamma_6 n(N) + \gamma_7 n(N_2)]. \tag{63}$$

This analysis shows that, in the *D*-region, the last term of the second member of equation (62) and (63) cannot be neglected when reactions (6) and (7) are involved. If the cross-section for reaction (7) reaches 10^{-20} cm^2, it may even play a role in the lower *E*-layer. When the transformation of O_2^+ into NO^+ can be ignored, it is clear from (62) and (63) that atmospheric conditions are simplified, since then one can write

$$n^+(\mathrm{NO})\{\alpha(\mathrm{NO})n_e\} = [1 - A]q(\mathrm{O}) + [1 - C][B - AB]q(\mathrm{N_2}) + q(\mathrm{NO}) \qquad (64)$$

and

$$n^+(\mathrm{O_2})\{\alpha(\mathrm{O_2})n_e\} = Aq(\mathrm{O}) + [1 - C][1 - (B - AB)]q(\mathrm{N_2}) + q(\mathrm{O_2}). \qquad (65a)$$

Application of (64) and (65a) in the *F1*-layer requires the knowledge of a large number of parameters. Numerous experimental and aeronomic data are needed before the whole ionosphere will be susceptible to explanation even under photo-equilibrium conditions. Note again that the conditions in the lower *E*-layer or upper *D*-region should not be studied by using an equation such as (65a) but, with (63) and (41), by

$$n^+(\mathrm{O_2})\{\alpha(\mathrm{O_2})n_e\} = D\{Aq(\mathrm{O}) + [1 - C][1 -(B - AB)]q(\mathrm{N_2}) + q(\mathrm{O_2})\} \qquad (65b)$$

with *A*, *B*, *C* and *D* between 0 and 1. Factor *D* may be small in the lower ionosphere and certainly reach unity in the *F1*-layer, *C* is small in the *E*-layer but does not reach unity in the *F1*-layer while *B* has its smallest value in the lower part of the ionosphere but increases with height; particularly in the diffusion region. A should decrease with height since $n(\mathrm{O_2})/n(\mathrm{N_2})$ decreases in the diffusion region.

In conclusion, the five equations (43), (48), (52), (62) and (65) show how each ion is related to the various productions $q(\mathrm{N_2})$, $q(\mathrm{O})$, $q(\mathrm{O_2})$, $q(\mathrm{NO})$ and $q(\mathrm{N})$. Any aeronomic analysis must deal with the vertical distribution of the various factors *A*, *B*, *C* and *D*. An exact knowledge of these factors requires a precise determination of the rate coefficients of reactions (1) and (2), (8) and (9), (6) and (7) and (12) with that of the recombination coefficients $\alpha(\mathrm{N_2})$, $\alpha(\mathrm{O_2})$ and $\alpha(\mathrm{NO})$, i.e. the knowledge of at least 10 parameters when the vertical distribution of neutral constituents (N_2, O_2, O and NO) with their ionization and absorption rate coefficients is perfectly known along with the solar flux. Since temperature effects are also important, it is clear that only approximate solutions can be obtained. Some simplification may be introduced when a specific ionospheric region is considered as shown in the analysis of the theoretical behavior of each ion. Nevertheless, the general complexity of equations (43) to (65) demonstrates that contradictory conclusions can be reached when a parameter is not well chosen. More *in situ* observations, particularly of ion densities are needed before sufficient aeronomic data will be available to determine rate coefficients of reactions yet unknown from laboratory measurements.

(7) *Hydrogen and helium ions*

It is not the purpose of this work to discuss the behavior of H^+ and He^+ ions which play an important role above the *F2*-peak where diffusion controls the electron and ion densities. However, it may be pointed out that charge transfer processes give the basic conditions(63). At sufficiently low altitudes, the photoionization of H is less important than the charge transfer $H + O^+ \rightarrow H^+ + O$. For atomic hydrogen ions, the steady state is given by

$$\frac{n^+(\mathrm{H})}{n^+(\mathrm{O})} = \frac{9}{8}\frac{n(\mathrm{H})}{n(\mathrm{O})} \qquad (66)$$

where the ratio 9/8 is the ratio of products of statistical weights considering

$$H + O^+ \rightleftharpoons H^+ + O \tag{67}$$

as the essential process. In the lower ionosphere, $n(H)/n(O)$ is small, less than 10^{-5}, and since $n^+(O) < n_e$ the concentration of atomic hydrogen ions is very small in the thermosphere. Above the *F2*-peak, the ratio $n(H)/n(O)$ increases and $n^+(O) \simeq n_e$. At high temperatures of the order of 2000°K $n(H)/n(O)$ is still of the order of 10^{-5}, and $n^+(H)$ is less than 10 cm^{-3}. However, the ratio $n(H)/n(O)$ is very sensitive to the temperature; it reaches, at 500 km, about 10^{-3} for $T = 1000°K$ and increases up to more than 10^{-1} at 700°K.(64) It is, therefore, clear that H^+ becomes an important ion near 1000 km when the temperature decreases to about 1000°K.

For helium ions, boundary conditions for the diffusive region are subject to the effect of its ionization by ultraviolet radiation. It will play an important role, when the temperature is sufficiently high ($T >$ 1000°K), only in the diffusive region and will remain a minor ion in normal ionospheric layers.

The quantitative effects of charge transfer above the *F2*-peak are unknown as yet so that the ratio $n^+(He)/n^+(O)$, in the region where $n^+(O) \gg n^+(He)$, is uncertain. Similarly, the ratio $n^+(N)/n^+(O)$ which depends on reaction (12) in the *E-F* layers may also be affected by the charge transfer process

$$N^+ + O \rightarrow O^+ + N \tag{68}$$

and (or)

$$N^+ + O_2 \rightarrow O_2^+ + N. \tag{69}$$

The formula

$$n^+(N) = \frac{n(N_2)I(N_2)}{\gamma_{68}n(O) + \gamma_{69}n(O_2)} \tag{70}$$

may define the lower boundary conditions for $n^+(N)$ better than equation (46) in the diffusion region where $n^+(N)/n^+(O) \leq 0{\cdot}1$. No rate coefficients for these processes are available.

Acknowledgement—The research reported in this work has been sponsored by the National Science Foundation under Grant G18983 and by the Geophysics Research Directorate of the Air Force Cambridge Research Laboratory, Air Research and Development Command under Contract Af19(604)-4563.

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Резюме—Сделан общий анализ ионосферных условий в связи с возможными ионными реакциями, имеющими место в атмосфере. Полученные данные о различных параметрах, как например производство и рекомбинация ионов, показывают, что необходимо иметь точное знание о спектральном распределении солнечного излучения и другие экспериментальные определения диссоциативных рекомбинаций.

Подчеркивают ионную сложность ионосферы описанием механизма реакций между O^+ и $И^+$ и молекулами $И_2$, O_2, и ИО. Поведение молекулярных ионов $И_2{}^+$, $O_2{}^+$ и $ИO^+$ зависит от группы одновременных процессов, включающих в себе зарядообмены и взаимные обмены ионов и атомов, которые являются более важными чем диссоциативные рекомбинеции. Приводят пример высотного распредедения ионов рассуждением относительной важности разных коэффициентов потерь в областях Д, Е и F. Показано, что молекулярные азотные ионы подчиняются важным процессам переноса заряда, и что ионы ИО–всегда конечные продукты, которые уничтожаются только диссоциативной рекомбинацией. Кроме того, целое производство ионов атомарного кислорода связано с фотоионизацией молекулярного азота. Дают тоже некоторые данные о возможных аномалиях в соотношении плотности $O_2{}^+$ и $ИO^+$ в нижней ионосфере. Из-за недостатка достаточной экспериментальной информации об ионных процессах показано, что точный анализ ионосферного поведения остается весьма сомнительным.