

POSITIVE ION REACTIONS AND PRODUCTIONS IN THE IONOSPHERE*

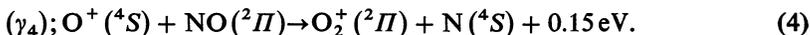
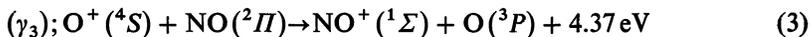
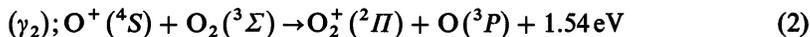
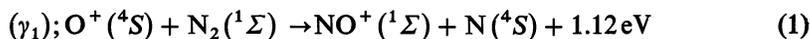
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1. Ionic Reactions

Starting from the observational knowledge of the ionosphere, 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 F_2 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:

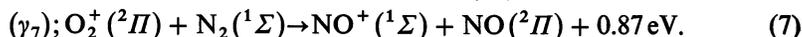
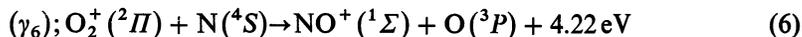
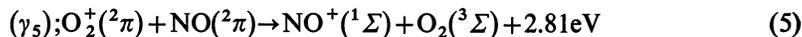


The following charge transfer process must be added as a production process.



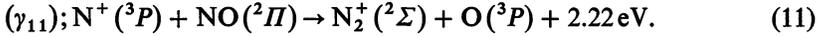
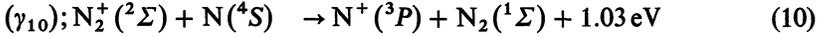
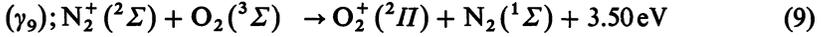
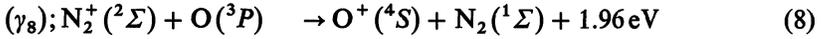
Similarly, a charge transfer process between O^+ and NO is equivalent to reaction (3).

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



* For a complete analysis with references, see NICOLET, M. and SWIDER Jr., W.: 1963, *Plan. Space Sci.* **11**, 12.

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



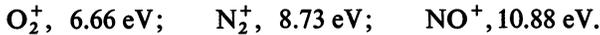
Finally, ion-atom interchange reactions in which N^+ and ON^+ are involved must be considered by taking into account that the lower state of ON^+ is the excited state $^3\Pi$ of the normal ion NO^+ .



Reactions which may occur in the ionosphere require that the excitation energy $E(^3\Pi)$ is less than the energy balance. Thus reactions (12) to (15) must be rejected since $E(^3\Pi)$ is more than 7 eV.

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

Dissociation of ionized molecules:



Dissociation of neutral molecules:



Ionization of neutral molecules:

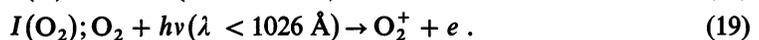


Ionization of neutral atoms:

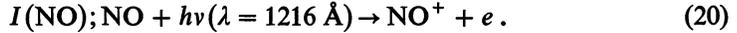


2. Photo-ionization Processes

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



The photo-ionization of NO is essentially due to the Lyman- α radiation at 1216 Å:



The 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 O₂, N₂ and O cannot be photo-ionized by λ 1216.7 Å. Other constituents such as Na ($\lambda < 2412$ Å), Ca ($\lambda < 2071$ Å), CH₃ ($\lambda < 1260$ Å), C ($\lambda < 1100$ Å) can be photo-ionized by radiations which are unable to ionize O₂.

(b) Ionization by X-rays of $\lambda < 10$ Å, i.e. with cross-sections less than 10^{-19} cm². 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 hundreds.

(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 of Lyman- α and cosmic rays as compared with the extremely varying source represented by X-rays.

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

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

i.e. with the following values: $\Phi = 0^\circ$, $1.25 \times 10^{-18} \text{ sec}^{-1}$; $\Phi = 30^\circ$, $2 \times 10^{-18} \text{ sec}^{-1}$; $\Phi = 40^\circ$, $4.5 \times 10^{-18} \text{ sec}^{-1}$; $\Phi = 50^\circ$, $1 \times 10^{-17} \text{ sec}^{-1}$ and $\Phi = 60^\circ$, $1.25 \times 10^{-17} \text{ sec}^{-1}$.

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

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

a small ratio $n(\text{NO})/n(\text{O}_2) = 10^{-10}$ leads to an electron production of the same order as the X-ray production under quiet solar conditions. Thus the 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 radiations 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. The variation with the solar cycle of these ultraviolet radiations should be less than a factor of two.

(b) Ionization by X-rays of $\lambda > 10 \text{ \AA}$ and particularly by the radiation in the spectral range $30 < \lambda < 100 \text{ \AA}$.

(c) Ionization of meteor atoms with low ionization potentials.

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 the ultraviolet radiation will have its maximum ionization effect under quiet solar conditions and, particularly, during the minimum of the solar cycle. The X-ray action will vary with solar activity and will become predominant during disturbed solar conditions.

(III) *F Region:*

(a) Ionization of molecular nitrogen for $\lambda < 796 \text{ \AA}$ with absorption cross-section greater than 10^{-17} cm^2 .

(b) Ionization of atomic oxygen for $\lambda < 796 \text{ \AA}$ subject to the absorption of molecular nitrogen.

(c) Ionization of atomic oxygen for $\lambda > 800 \text{ \AA}$ with different absorption cross-sections for its different ionization potentials at 910 \AA , 732 \AA and 665 \AA .

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, N₂ and O₂. 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.

3. 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 photo-ionization 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 $X^+ \text{ (or } XY^+) + e \rightarrow X \text{ (or } XY) + h\nu$. Since the recombination coefficient is always between 1×10^{-12} and $5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ in the ionosphere, the radiative recombination is negligible compared with other processes affecting ions. Three-body electronic or ionic recombination processes are also negligible 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:



(the * indicating possible excitation). It is clear from the theoretical analysis that it is practically impossible to predict the temperature variation of the dissociative recombination coefficient, α . In other words, if values of α between 10^{-6} and 10^{-9} cm^3

sec⁻¹ and variations with temperatures such as $T^{-1 \pm 0.5}$ are assumed, they do not contradict theoretical considerations. 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:



Various experimental determinations of the recombination coefficients of these three ions exist, but it is difficult to adopt a correct value for ionospheric purposes. Obviously, a temperature dependence has been introduced in order to follow ionospheric observations, but a coefficient varying with $T^{-1 \pm 0.5}$ leads to very different values in the F layer.

The night-time conditions should give a value of the recombination coefficient in the E and F₁ regions. 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.

Electron concentrations of the order of 10^3 cm^{-3} below the F₂ region require an electron recombination coefficient of the order of $2.5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ for a predominant ion such as NO^+ , or the presence of meteor-ions with radiative recombination coefficients. A value of α reaching $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ cannot result in more than 2.5×10^2 electrons at the end of the night. Nevertheless, types of E_S ionization could modify the analysis since the 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. 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.

4. Analysis of Ionospheric Reactions

A. GENERAL CONDITIONS

All processes (1) to (21) (after neglecting the effect of negative ions) must be considered in order to determine the essential reactions in the ionosphere. 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 to 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 $n^+(\text{O}_2)/n^+(\text{NO})$ is

not independent of reactions leading to O^+ or NO^+ , since O_2^+ may transform into NO^+ by ion interchange reactions (γ_7 and γ_6).

B. EQUILIBRIUM CONDITIONS

In order to determine the relative importance of reactions (1) to (21), ionization equations are first considered for steady state conditions. They may be written as follows:

$$n^+(\text{N}_2) = \frac{n(\text{N}_2)I(\text{N}_2) + n^+(\text{N})\gamma_{11}n(\text{NO})}{\alpha(\text{N}_2)n_e + \gamma_8n(\text{O}) + \gamma_9n(\text{O}_2) + \gamma_{10}n(\text{N})} \quad (22)$$

$$n^+(\text{N}) = \frac{n(\text{N}_2)I_2(\text{N}) + n(\text{N})[I(\text{N}) + \gamma_{10}n^+(\text{N}_2)]}{\gamma_{12}n(\text{O}_2) + [\gamma_{11} + \gamma_{13}]n(\text{NO})} \quad (23)$$

$$n^+(\text{O}) = \frac{n(\text{O})[I(\text{O}) + \gamma_8n^+(\text{N}_2)]}{\gamma_1n(\text{N}_2) + \gamma_2n(\text{O}_2) + [\gamma_3 + \gamma_4]n(\text{NO})} \quad (24)$$

$$n^+(\text{O}_2) = \frac{n(\text{O}_2)[I(\text{O}_2) + \gamma_2n^+(\text{O}) + \gamma_9n^+(\text{N}_2)] + n(\text{NO})\gamma_4n^+(\text{O})}{\alpha(\text{O}_2)n_e + \gamma_6n(\text{N}) + \gamma_7n(\text{N}_2)} \quad (25)$$

$$n^+(\text{NO}) = \frac{1}{\alpha(\text{NO})n_e} \{n^+(\text{O})[\gamma_1n(\text{N}_2) + \gamma_3n(\text{NO})] + n^+(\text{O}_2) \cdot [\gamma_6n(\text{N}) + \gamma_7n(\text{N}_2)] + n^+(\text{N})[\gamma_{12}n(\text{O}_2) + \gamma_{13}n(\text{NO})] + n(\text{NO})I(\text{NO})\}. \quad (26)$$

An adequate approximation for (22) to (26) is introduced by neglecting reactions (3), (4), (11) and (13) in that $\gamma n(\text{NO}) \ll \gamma n(\text{O}_2)$ or $\gamma n(\text{N}_2)$.

In all the ionization equations (22) to (26) 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:

$$A = \frac{\gamma_2n(\text{O}_2)}{\gamma_1n(\text{N}_2) + \gamma_2n(\text{O}_2)}; \quad 1 - A = \frac{\gamma_1n(\text{N}_2)}{\gamma_1n(\text{N}_2) + \gamma_2n(\text{O}_2)} \quad (27)$$

(b) for production of atomic oxygen ions,

$$B = \frac{\gamma_8n(\text{O})}{\gamma_8n(\text{O}) + \gamma_9n(\text{O}_2)}; \quad 1 - B = \frac{\gamma_9n(\text{O}_2)}{\gamma_8n(\text{O}) + \gamma_9n(\text{O}_2)} \quad (28)$$

(c) for loss of molecular nitrogen ions,

$$C = \frac{\alpha(\text{N}_2)n_e}{\alpha(\text{N}_2)n_e + \gamma_8n(\text{O}) + \gamma_9n(\text{O}_2)}; \quad 1 - C = \frac{\gamma_8n(\text{O}_2) + \gamma_9n(\text{O}_2)}{\alpha(\text{N}_2)n_e + \gamma_8n(\text{O}_2) + \gamma_9n(\text{O}_2)} \quad (29)$$

(d) for loss of molecular oxygen ions,

$$D = \frac{\alpha(\text{O}_2)n_e}{\alpha(\text{O}_2)n_e + \gamma_6n(\text{N}) + \gamma_7n(\text{N}_2)}; \quad 1 - D = \frac{\gamma_6n(\text{N}) + \gamma_7n(\text{N}_2)}{\alpha(\text{O}_2)n_e + \gamma_6n(\text{N}) + \gamma_7n(\text{N}_2)}. \quad (30)$$

C. MOLECULAR NITROGEN ION

The ion N_2^+ is a minor constituent in the ionosphere even if its production by ultra-violet radiation $n(N_2)I(N_2)=q(N_2)$ is important. Equation (22) becomes, after making the approximations justified before,

$$n^+(N_2) = \frac{q(N_2)}{\alpha(N_2)n_e + \gamma_8 n(O) + \gamma_9 n(O_2)} \quad (31)$$

showing that various loss processes dominate, depending on the altitude involved.

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 the equation (29) is needed.

D. ATOMIC NITROGEN ION

Atomic nitrogen is a minor constituent and its ion, N^+ , exists only above the F_1 layer, being a certain fraction of O^+ ($< 10\%$) in the F_2 layer. The N^+ concentration is given essentially by the following approximation of (23):

$$n^+(N) = \frac{n(N_2)I_2(N) + n(N)[I(N) + \gamma_{10}n^+(N_2)]}{\gamma_{12}n(O_2) + \gamma_{16}n(O)} \quad (32)$$

The principal loss process of N^+ occurs by ion-atom interchange reactions with O_2 which apparently is very rapid, or by the generally adequate approximation,

$$n^+(N) = \frac{n(N_2)I_2(N)}{\gamma_{12}n(O_2) + \gamma_{16}n(O)} \quad (33)$$

E. ATOMIC OXYGEN IONS

The principal reactions in which O^+ is involved lead to the following equation for photo-ionization equilibrium, (24)

$$n^+(O)_{eq} = \frac{q(O) + n^+(N_2)\gamma_8 n(O)}{\gamma_1 n(N_2) + \gamma_2 n(O_2)} \quad (34)$$

or

$$n^+(O)_{eq} = \frac{q(O) + B(1 - C)q(N_2)}{\gamma_1 n(N_2) + \gamma_2 n(O_2)} \quad (35)$$

in which $0 \leq B \leq 1$.

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 F_1 layer. Thus, there is a contribution to the direct photo-ionization of atomic oxygen by the indirect photo-ionization 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 day-time conditions in the F_1 layer according to ionospheric observations, they must be rejected for the F_2 layer. Daytime and nighttime conditions for F_1 and F_2 layers clearly show that the loss coefficient

$$\gamma_1 n(N_2) + \gamma_2 n(O_2) = \beta(z) \quad (36)$$

becomes small so that

$$n^+(O) = n^+(O)_{t=0} e^{-\beta(z)t} + n^+(O)_{eq} [1 - e^{-\beta(z)t}]. \quad (37)$$

In other words, the low electron concentration in the F_1 layer for night-time conditions means that the principal loss processes (1) and (2) for atomic oxygen ions are large, and that steady state conditions can be used for day-time conditions. In the F_2 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 F_2 peak and is active above it, so that photoequilibrium cannot be applied in that region.

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.

F. MOLECULAR IONS O_2^+ AND NO^+

Mass-spectrometric measurements show that O_2^+ and NO^+ are the principal ions in the E layer and that O^+ becomes important only in the F_1 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, (25) and (26) are written as follows:

$$n^+(NO) \{ \alpha(NO) n_e \} = q(NO) + [1 - A] [\gamma_1 n(N_2) + \gamma_2 n(O_2)] n^+(O) + [\gamma_6 n(N) + \gamma_7 n(N_2)] n^+(O_2) \quad (38)$$

$$n^+(O_2) \{ \alpha(O_2) n_e + \gamma_6 n(N) + \gamma_7 n(N_2) \} = q(O_2) + A [\gamma_1 n(N_2) + \gamma_2 n(O_2)] n^+(O) + [1 - B] [\gamma_8 n(O) + \gamma_9 n(O_2)] n^+(N_2). \quad (39)$$

Equations (38) and (39) 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 (27) 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^+ .

There is, therefore, an important problem to be resolved before determining the exact behavior of the upper D region and lower E layer.

Analysis of (39) shows that the direct production of O_2^+ ions by photoionization is an important process since all solar radiation of $\lambda < 1026 \text{ \AA}$ is involved. But the final

concentration $n^+(\text{O}_2)$ is related to the effect of its transformation into NO^+ by reactions (6) and (7). Above a certain altitude, (39) leads to

$$\frac{n^+(\text{O}_2)}{n^+(\text{O})} \geq \frac{\gamma_2 n(\text{N}_2) + q(\text{O}_2)/n^+(\text{O})}{\alpha(\text{O}_2) n_e} \quad (40)$$

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

$$n^+(\text{O}_2) \geq \frac{q(\text{O}_2)}{\alpha(\text{O}_2) n_e} + \frac{\gamma_2 n(\text{O}_2)}{\alpha(\text{O}_2)}. \quad (41)$$

Equations (40) and (41) should be applied to the F_1 and F_2 layers, respectively; O_2^+ production depends on the ion-atom interchange reaction (2) together with direct photoionization.

The general ionization equations (38) and (39) can be written, using equilibrium conditions (41) and (35),

$$n^+(\text{NO}) \{ \alpha(\text{NO}) n_e \} = q(\text{NO}) + [1 - A] q(\text{O}) + [1 - C] [B - AB] q(\text{N}_2) + n^+(\text{O}_2) [\gamma_6 n(\text{N}) + \gamma_7 n(\text{N}_2)] \quad (42)$$

and

$$n^+(\text{O}_2) \{ \alpha(\text{O}_2) n_e \} = q(\text{O}_2) + Aq(\text{O}) + [1 - C] [1 - (B - AB)] q(\text{N}_2) - n^+(\text{O}_2) [\gamma_6 n(\text{N}) + \gamma_7 n(\text{N}_2)]. \quad (43)$$

This analysis shows that the last term of the second member of equation (42) and (43) cannot be neglected when reactions (6) and (7) are involved. When the transformation of O_2^+ and NO^+ can be ignored, it is clear from (42) and (43) that atmospheric conditions are simplified, since then one can write:

$$n^+(\text{NO}) \{ \alpha(\text{NO}) n_e \} = [1 - A] q(\text{O}) + [1 - C] [B - AB] q(\text{N}_2) + q(\text{NO}) \quad (44)$$

and

$$n^+(\text{O}_2) \{ \alpha(\text{O}_2) n_e \} = Aq(\text{O}) + [1 - C] [1 - (B - AB)] q(\text{N}_2) + q(\text{O}_2). \quad (45)$$

Application of (44) and (45) in the F_1 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.

In conclusion, the five equations (31), (33), (34), (44) and (45) show how each ion is related to the various productions $q(\text{N}_2)$, $q(\text{O})$, $q(\text{O}_2)$, $q(\text{NO})$ and $q(\text{N})$. 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 $\alpha(\text{N}_2)$, $\alpha(\text{O}_2)$ and $\alpha(\text{NO})$, 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 coefficient is known with accuracy, 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 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.