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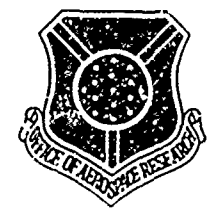
**AIR FORCE CAMBRIDGE RESEARCH LABORATORIES**  
L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

# A Technique for Solving the General Reaction-Rate Equations in the Atmosphere

THOMAS J. KENESHEA

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UPPER ATMOSPHERE PHYSICS LABORATORY PROJECT 8605

## AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

# A Technique for Solving the General Reaction-Rate Equations in the Atmosphere

THOMAS J. KENESHEA

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## Abstract

With the availability of numerical techniques for solving an extensive set of nonlinear differential equations and high-speed computers for performing the calculations, interest in solving the unrestricted reaction-rate equations is growing among ionospheric researchers. In view of this, the author has continued to refine the techniques that he previously developed.

The computer code, as discussed here, is written to solve the photochemical behavior of 15 atmospheric species; these species are electrons,  $O^-$ ,  $O_2^-$ ,  $O_3^-$ ,  $NO_2^-$ ,  $O^+$ ,  $O_2^+$ ,  $N_2^+$ ,  $NO^+$ ,  $NO$ ,  $N$ ,  $NO_2$ ,  $O_3$ ,  $N_2O$ , and  $O$ . Built into the code are 168 reactions that can conceivably take place among these constituents. Several examples of the results obtained using the code are presented, including the buildup of ionization from zero concentrations at altitudes in the D and E regions and the deionization of an atmosphere with high initial electron densities. The diurnal variation of the atmospheric constituents is also presented along with profiles for the above-mentioned species from 60 km to 120 km.

The computer codes are included in their entirety with complete explanations on their usage.

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## Tables

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| 1. Solar Flux Data, Ionization Cross Sections, and Absorption Cross Sections | 53 |
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## A Technique for Solving the General Reaction-Rate Equations in the Atmosphere

### 1. INTRODUCTION

The capability of solving the set of differential equations that describe the time dependence of individual atmospheric constituents is becoming more and more important to ionospheric research. Modification and extension of the computer techniques that were developed by the author (1962, 1963) have continued because of this. Since in certain applications these techniques could not generate solutions and since these applications are important to ionospheric studies, the techniques were reevaluated in order to make their usefulness more general.

The most significant change made in the code is the handling of the solution for a species after it has gone into equilibrium or into quasi-equilibrium with one or more other species. The techniques involved in developing a solution under these conditions have always presented problems. The algebraic equations that were used in previous work for the computation of the concentrations of the species in equilibrium or quasi-equilibrium proved to be inadequate for this purpose. A new approach that lead to a set of exponential equations which replaced the set of algebraic equations was developed involving less stringent restrictions. With this new technique, no code failures were experienced.

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Another important change is in the method of numerically integrating the differential equations. Although it develops stable solutions, the Runge Kutta technique used previously is uneconomical in terms of computer time. In order to reduce the amount of computer time required for each solution, the Runge Kutta technique was replaced by the Kutta Merson technique. This later method requires fewer computations of the derivatives over each increment thereby conserving computer time.

Other changes include removal of the sum equations used by the author (1963) since the reason for their being employed was eliminated with the new technique for solving the concentrations of the species in equilibrium, the computation of the largest negative species from charge balance rather than the largest positive species, the use of a separate code to write the subprogram SLOP which computes the values of the derivatives, and the inclusion in the code of two additional species (nitrogen peroxide and atomic oxygen) along with 25 new reactions.

The updated codes are presented here with several practical applications. These examples include the simple buildup of ionization from zero by an external source, the deionization from high initial conditions and the diurnal variation of the atmospheric species in the D and E regions.

## 2. REVISIONS IN THE TECHNIQUES OF SOLUTION

Since the last report by the author (1963) was written, attempts were made to use the code under diversified conditions. In several of these instances, the code either failed to generate realistic solutions or was unable to generate any solution at all; the source of this trouble was always traced back to the solution of the algebraic set of equations. This set of simultaneous algebraic equations was used to compute the concentrations of the species that are in quasi-equilibrium. Using a criterion of  $10^{-2}$  on the iterations of the algebraic set allowed a certain amount of charge imbalance to be accepted. Because the major positive ion was always being computed from the requirement of balance of charge, any charge imbalance resulting from the solution of the algebraic equations was attributed to this positive ion. As long as this positive ion remained the most abundant throughout the solution, this allowed imbalance did not cause any noticeable problems. Whenever another positive ion became the most abundant, however, the program generally was incapable of advancing the solution. Once a positive ion was superceded as the dominant ion, it was no longer computed from the requirement of charge balance but rather from its differential equation. Since the concentration of this ion had taken up the excess charge that was allowed to creep into the solution, the value of its density was not consistent with that obtained from the solution of its differential equation. The program tried to correct



this situation but the damage was irreparable and the program was forced to maintain a constant mesh of the order of a microsecond.

The simple act of tightening the criterion on the iterations of the algebraic set to  $10^{-4}$  and thus reducing the allowed charge imbalance removed this problem from practical concern. The resulting greater accuracy in the solution of the algebraic equations also permitted the removal of the two sum equations used in the previous code. This change did not solve all of the problems, however.

Occasions arose where it appeared that at some point in the solution neither the differential set nor the algebraic set of equations could generate a solution. The code advanced the solution to a time at which it determined that a species was in quasi-equilibrium. It removed its differential equation from the set and expected a solution from the algebraic set of equations. However, the simultaneous solution of the algebraic equations did not converge in the fixed number of iterations. The code then demanded that the differential equation for this species be used for the solution. In order to obtain a solution from the differential equation at this point, however, it was necessary to reduce the integrating increment. The overall effect of this behavior was to allow the solution to advance but only in very small increments.

This difficulty was attributed to the fact that the species was in quasi-equilibrium and not in true equilibrium. In other words, its derivative was not zero as assumed in deriving the algebraic equations. If the differential equations are written as

$$\frac{dN_i}{dt} = \sum F_j - N_i \sum R_j \quad (1)$$

and if  $\frac{dN_i}{dt} = 0$ , then

$$N_i = \frac{\sum F_j}{\sum R_j} \quad (2)$$

This is the formula previously used to construct the set of algebraic equations. Because the derivative was not near zero, it could not be expected that the concentration could be computed from Eq.(2). In order to overcome this problem, the assumption that the derivative is zero was replaced by the more realistic assumption that the formation term  $\sum F_j$  and the removal term  $\sum R_j$  in Eq.(1) are constants. Equation (1) under these circumstances is a first order linear differential equation with constant coefficients and its exact solution is

$$N_i = \left( N_o - \frac{\sum F_j}{\sum R_j} \right) e^{-\sum R_j \cdot \Delta t} + \frac{\sum F_j}{\sum R_j} \quad (3)$$

where  $\Delta t$  is the length of the increment currently being used by the integrator and  $N_o$  is the concentration of the species at the beginning of this increment. Equation (3) is now used to construct the set of simultaneous exponential equations for the solution of the species that are in quasi-equilibrium.

The technique used by the author (1962, 1963) for numerically integrating the differential equations is the classical Runge Kutta fourth-order process. One of the disadvantages of this technique is that it does not contain within itself any measure of the accuracy of the solution at each integration. In order to impose some control on the accumulation of errors, three separate integrations are performed for a given increment. The first integration is made over the increment  $\Delta t$  starting with the concentrations  $N_i(t_o)$ ; the second integration is made over the increment  $\Delta t$  starting with the concentrations  $N_i(t_o + \Delta t)$ ; and, the third integration is made over the increment  $2\Delta t$  starting with the concentrations  $N_i(t_o)$ . The concentrations obtained after the second and third integration are compared; if they differ by more than some preset amount, the solution is considered to be invalid. This procedure requires 12 separate computations of the derivatives. The differential equations solved here generally contain a very large number of terms which means that a great deal of computer time is spent in computing the derivatives. This is very costly of machine time since in many cases the solution is unacceptable and the procedure must be repeated with a smaller increment.

Merson (1957) developed a technique based upon that of Kutta in which only five values of the derivative are required for any one solution. Since it appeared that this could be a great device for reducing the amount of computer time required for each solution, the Runge Kutta technique was replaced by the Kutta Merson technique. A detailed description of this method is given in Section 7.1.2.

### 3. CHEMICAL REACTIONS AND REACTION-RATE CONSTANTS

The computer code, as presented here, was written to evaluate the time histories of 15 variable atmospheric species: electrons,  $O^-$ ,  $O_2^-$ ,  $O_3^-$ ,  $NO_2^-$ ,  $O^+$ ,  $O_2^+$ ,  $N_2^+$ ,  $NO^+$ ,  $NO$ ,  $N$ ,  $NO_2$ ,  $O_3$ ,  $N_2O$ , and atomic oxygen. The model contains reservoirs of molecular oxygen and molecular nitrogen that are allowed to vary during

the solution in order to insure conservation of the total number of oxygen and nitrogen atoms initially present in the system.

The code contains 168 chemical reactions that can possibly take place among the variable species. With a few exceptions, the chemical processes and their rate constants incorporated into the code are those suggested by Bortner (1965). These rates are a combination of laboratory, insitu, theoretical, and estimated values. Although individual rate constants may certainly be subject to argument, they appear to be a reasonable collection and about the only suitable source to use in a program of this magnitude. The values used for the rate constants are generally the middle values within the range of uncertainty (Bortner, 1965). Deviations are made from this general rule in certain instances as in the case of the positive ion-charge transfer and charged rearrangement processes (Ferguson, Fehsenfeld, Goldan, and Schmeltokopf, 1965). Certain other rate constants were modified within the estimated error bounds (Bortner, 1965). These modifications represent minor adjustments that were found to produce results appearing to be more reasonable when compared with ionospheric measurements.

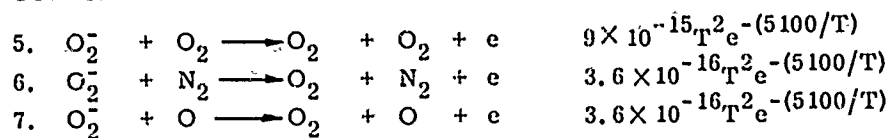
Some of the reactions in the following list produced products for which there are no differential equations in the set. In order to insure that these reactions do not remove from the system any of the charge for which account cannot be made, their rate constants are set to zero. This is equivalent to assuming that the reactions are relatively unimportant. There are also several reactions in the list that are probably unimportant in most ionospheric studies; but, since it is generally impossible to predetermine the importance of a given reaction and since it is the author's purpose to keep the code as general as possible, all reactions are retained in the code.

The following is the basic list of reactions and rate constants built into the code. The dimensions are  $\text{sec}^{-1}$ ,  $\text{cm}^3 \text{sec}^{-1}$ , and  $\text{cm}^6 \text{sec}^{-1}$  respectively for one, two, and three body reactions. The third body M is assumed to be  $\text{N}_2 + \text{O}_2$ . The temperatures used in computing the rate constants are taken from the U. S. Standard Atmosphere (1962). Those reactions marked with an asterisk have assumed rate constants other than those shown in some of the applications presented here.

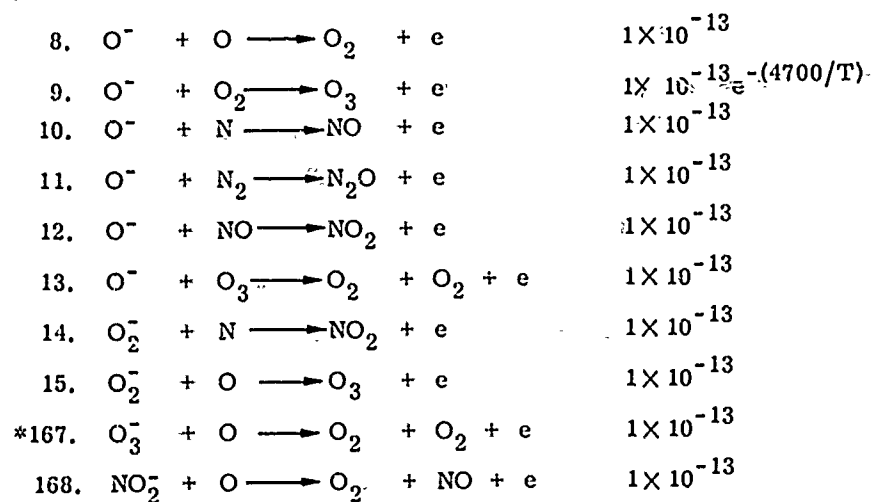
#### A. PHOTODETACHMENT

- |     |  |      |
|-----|--|------|
| 1.  | $\text{O}_2^- + h\nu \rightarrow \text{O}_2 + e$   | 0.44 |
| 2.  | $\text{O}^- + h\nu \rightarrow \text{O} + e$       | 1.4  |
| 3.  | $\text{NO}_2^- + h\nu \rightarrow \text{NO}_2 + e$ | 0.04 |
| *4. | $\text{O}_3^- + h\nu \rightarrow \text{O}_3 + e$   | 0.04 |

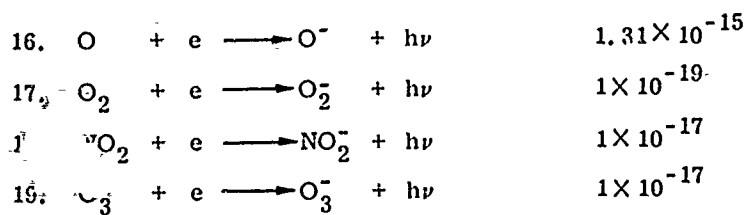
## B. COLLISIONAL DETACHMENT



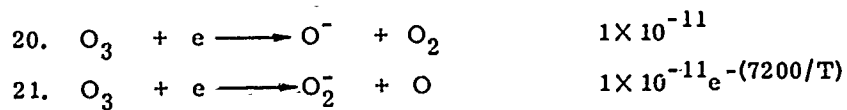
## C. ASSOCIATIVE DETACHMENT



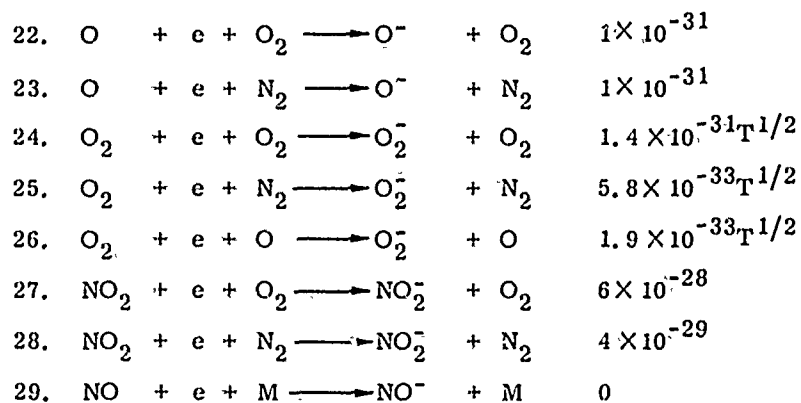
## D. RADIATIVE ATTACHMENT



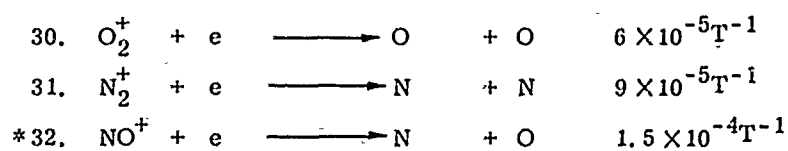
## E. DISSOCIATIVE ATTACHMENT



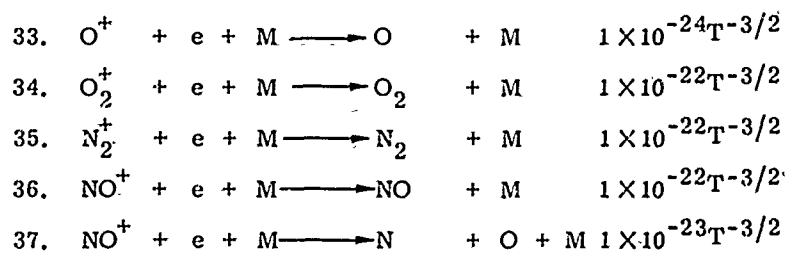
## F. THREE-BODY ATTACHMENT



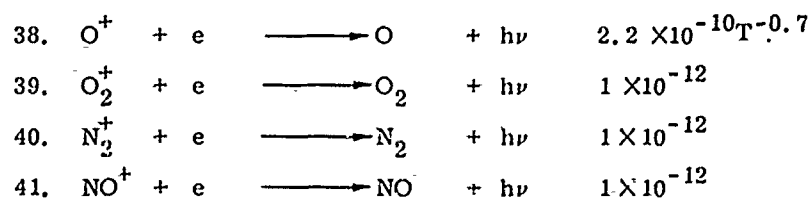
## G. DISSOCIATIVE RECOMBINATION



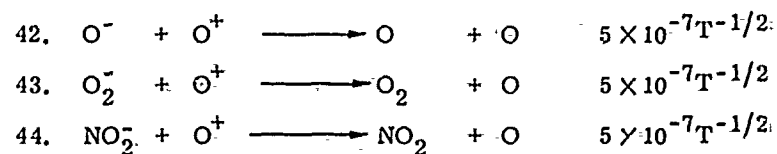
## H. THREE-BODY RECOMBINATION

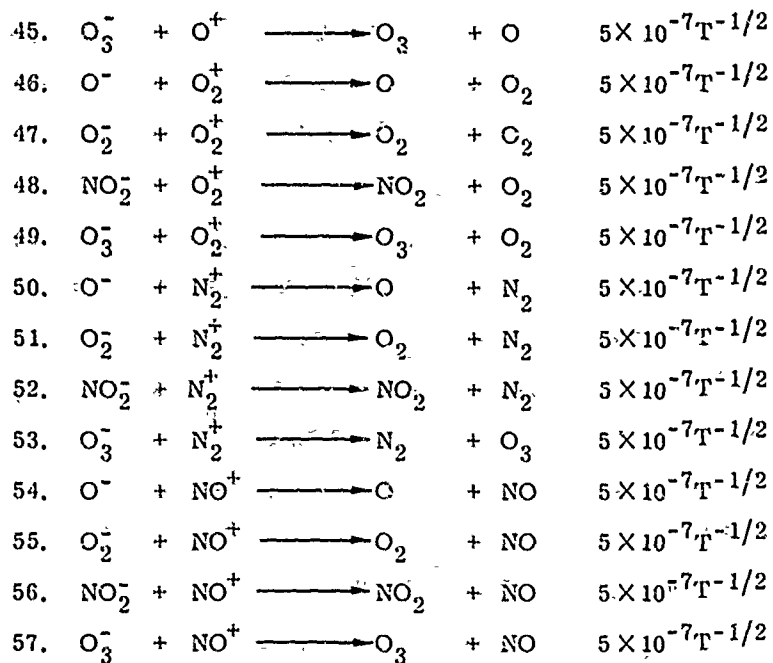


## I. RADIATIVE RECOMBINATION

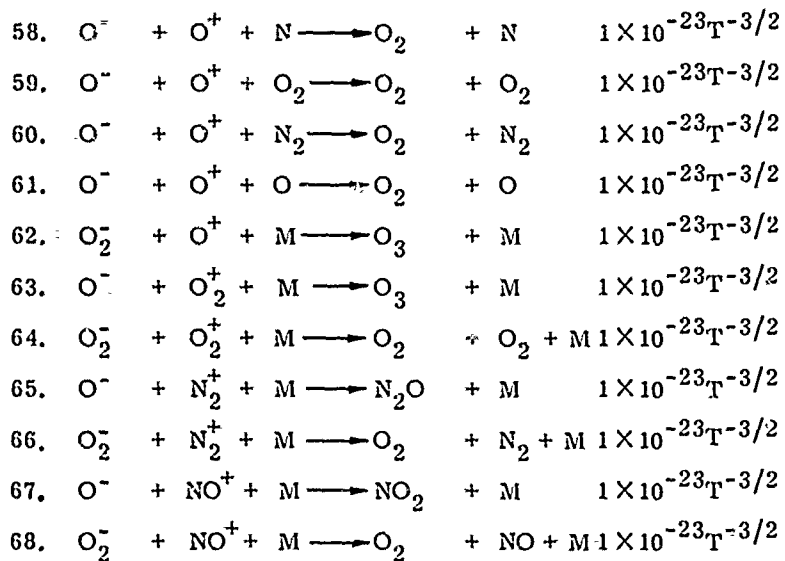


## J. ION-ION MUTUAL NEUTRALIZATION

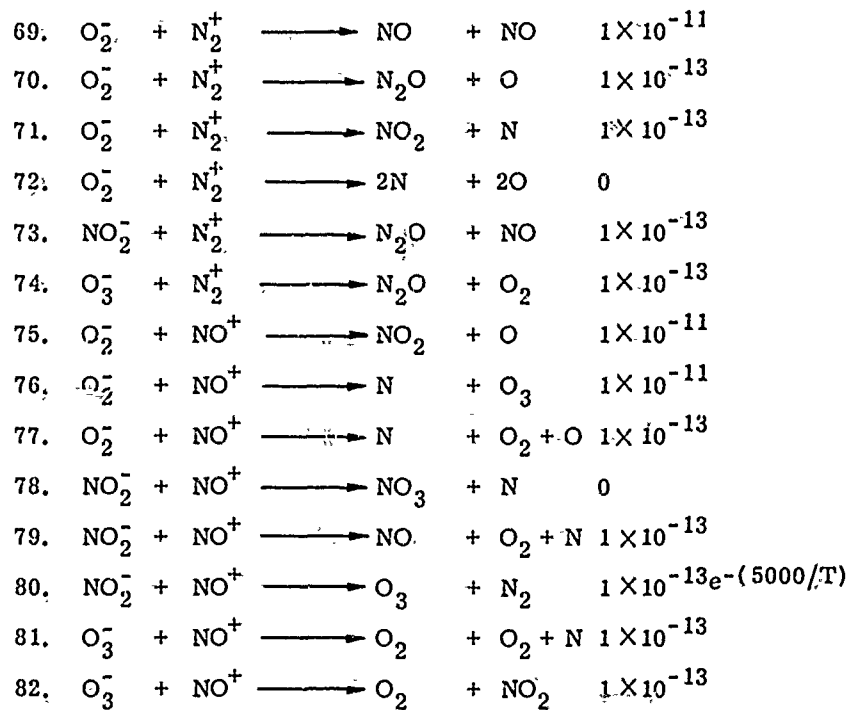




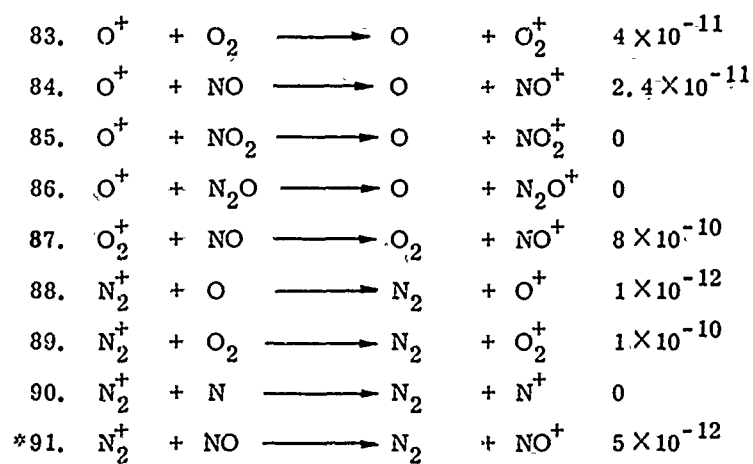
## K. THREE-BODY ION-ION RECOMBINATION



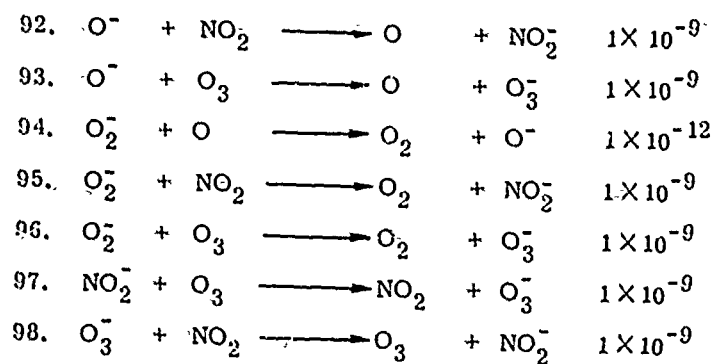
## L. ION-ION NEUTRALIZATION WITH REARRANGEMENT



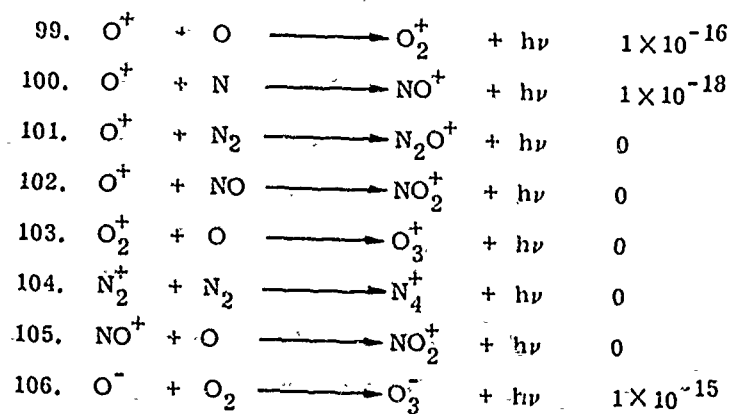
## M. POSITIVE CHARGE TRANSFER



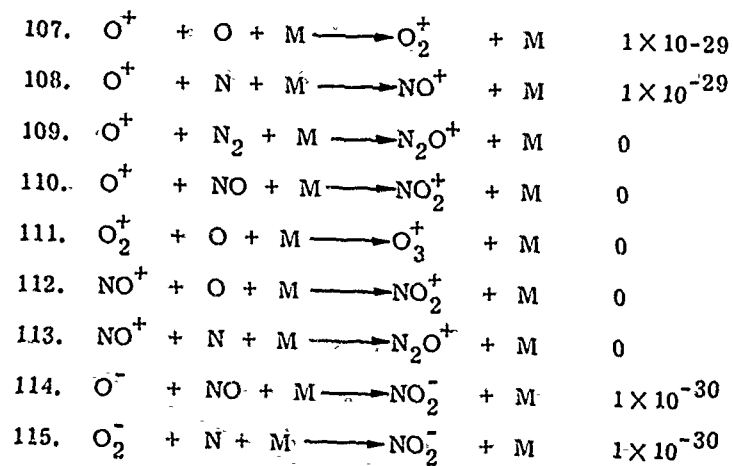
## N. NEGATIVE CHARGE TRANSFER



## O. ION-NEUTRAL ASSOCIATION-TWO BODY

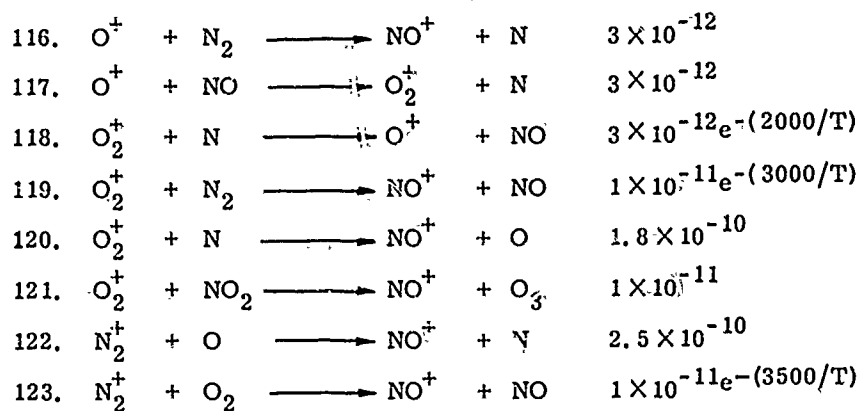


## P. ION-NEUTRAL ASSOCIATION-THREE BODY

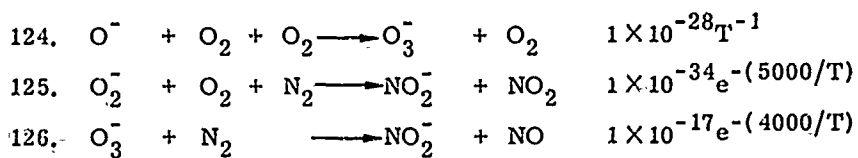




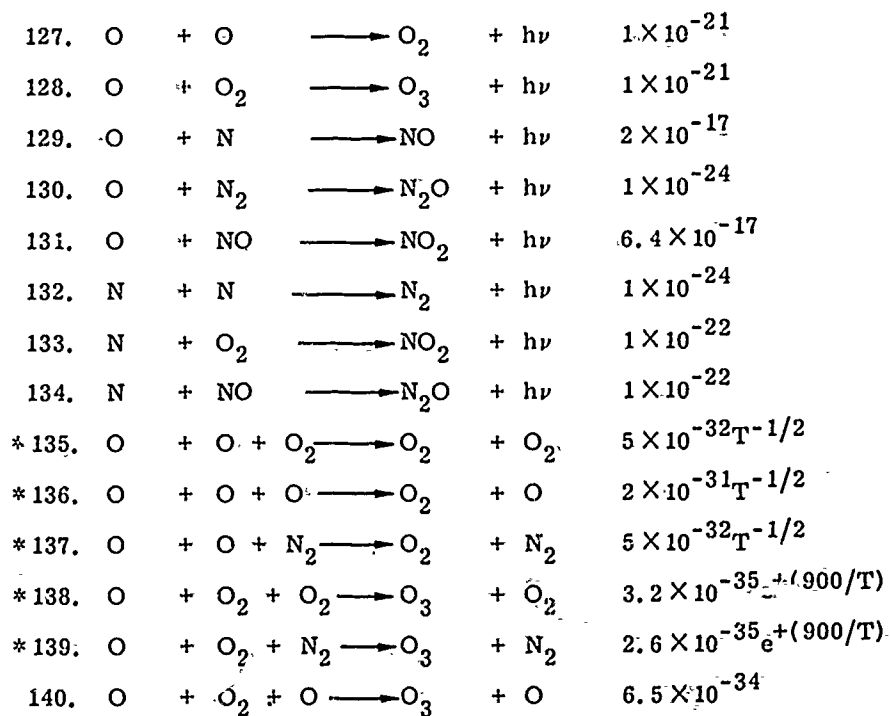
## Q. CHARGED REARRANGEMENT-POSITIVE ION

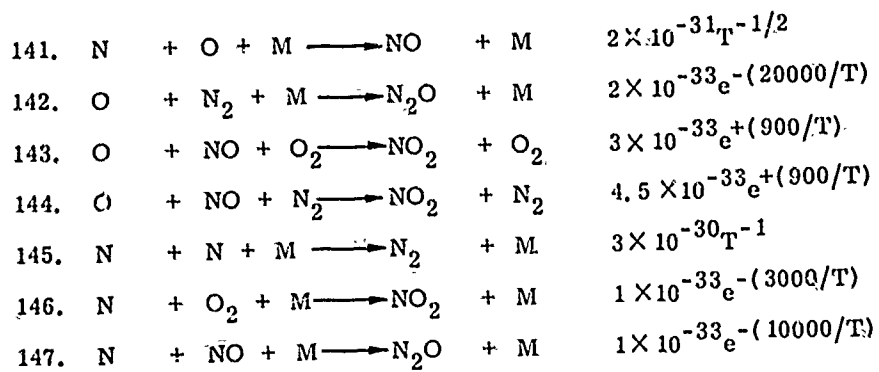


## R. CHARGED REARRANGEMENT-NEGATIVE ION

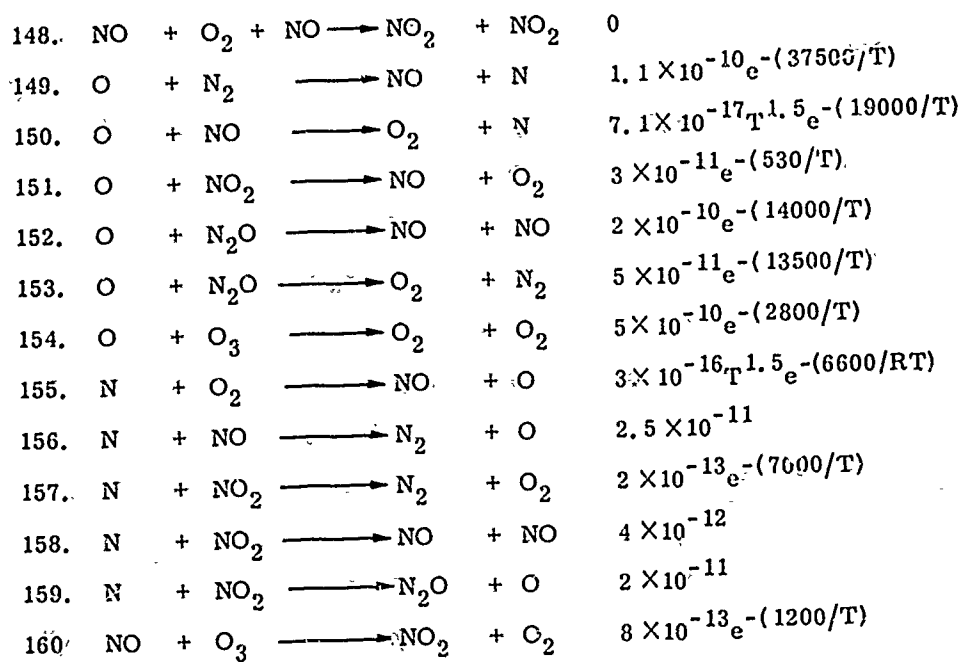


## S. TWO-BODY ATOM RECOMBINATION

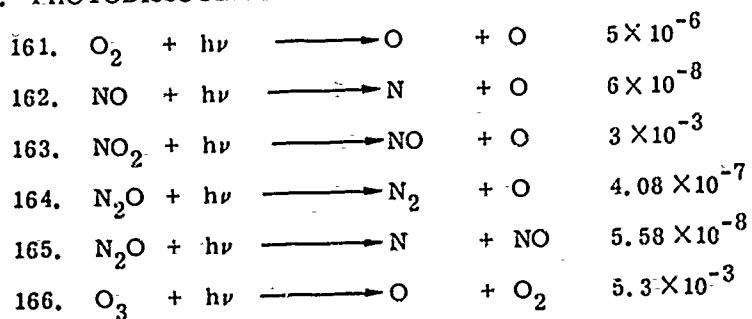




## U. NEUTRAL REARRANGEMENT



## V. PHOTODISSOCIATION



#### 4. APPLICATION OF THE CODE TO THE DEIONIZATION PROBLEM

The code, as described in Section 7. 1, was used to generate solutions to the differential equations under many different conditions. Four examples of a simple application were selected and the results obtained are presented here. Two of these describe the buildup of ionization from zero concentrations of the charged species with a continuing constant source at altitudes in the D and E regions. The remaining two describe the decay of ionization at these same altitudes from high initial values of electrons and positive ions with a small continuing source. The altitudes chosen are 70 km and 110 km.

Some changes were made in the basic list of rate constants given in Section 3. Ferguson, et al. (1965) have determined that the rate of the charge transfer reaction  $N_2^+ + NO \rightarrow NO^+ + N_2$  is much faster than previously thought. Their value of  $5 \times 10^{-10}$  is used for this process instead of  $5 \times 10^{-12}$ . For reasons that are discussed in Section 5.3, the  $NO^+$  dissociative recombination rate constant was changed to  $6 \times 10^{-5} T^{-1}$  to make it equal to the  $O_2^+$  dissociative recombination rate constant. The rate constants for the three-body recombination reactions Nos. 135, 136, and 137 were changed to  $2.7 \times 10^{-33}$  and the rate constants for reactions Nos. 138 and 139 were changed to  $3.7 \times 10^{-34} e^{-151}$ . Since these five reactions are important processes for the removal of atomic oxygen, adjustment of their rate constants was necessary in order to obtain a reasonable behavior of the atomic-oxygen concentration in the D region. In the examples presented here, the associative detachment reaction  $O_3^- + O \rightarrow O_2 + O_2 + e$  is important for the establishment of the negative ion to electron ratio in the D region. With all other important rate constants remaining unchanged, the rate constant for this process was increased to  $5 \times 10^{-11}$  in order to obtain a ratio of unity at 70 km. All other rate constants used in runs to be discussed in this section are as given in the above list.

Figure 1 shows the solution at 70 km with zero initial concentrations of all the charged species and with estimated initial concentrations of the minor neutral species. The continuing source creates 1.122 ion-pairs/cm<sup>3</sup>/sec. The production subroutine was set up to ionize the neutral species as if the source were UV radiation. Therefore,  $O_2^+$  is the most abundantly produced positive ion. For this demonstration of the functioning of the computer code, it is immaterial that the assumed production was unrealistic because in the D region  $L_\alpha$  and cosmic rays are actually the ionizing agents.

The atomic oxygen concentration remains constant until  $10^{-2}$  secs when the photodissociation of  $O_2$  and  $O_3$  becomes effective in producing this atom. The time constant for its removal by the three-body recombination reaction

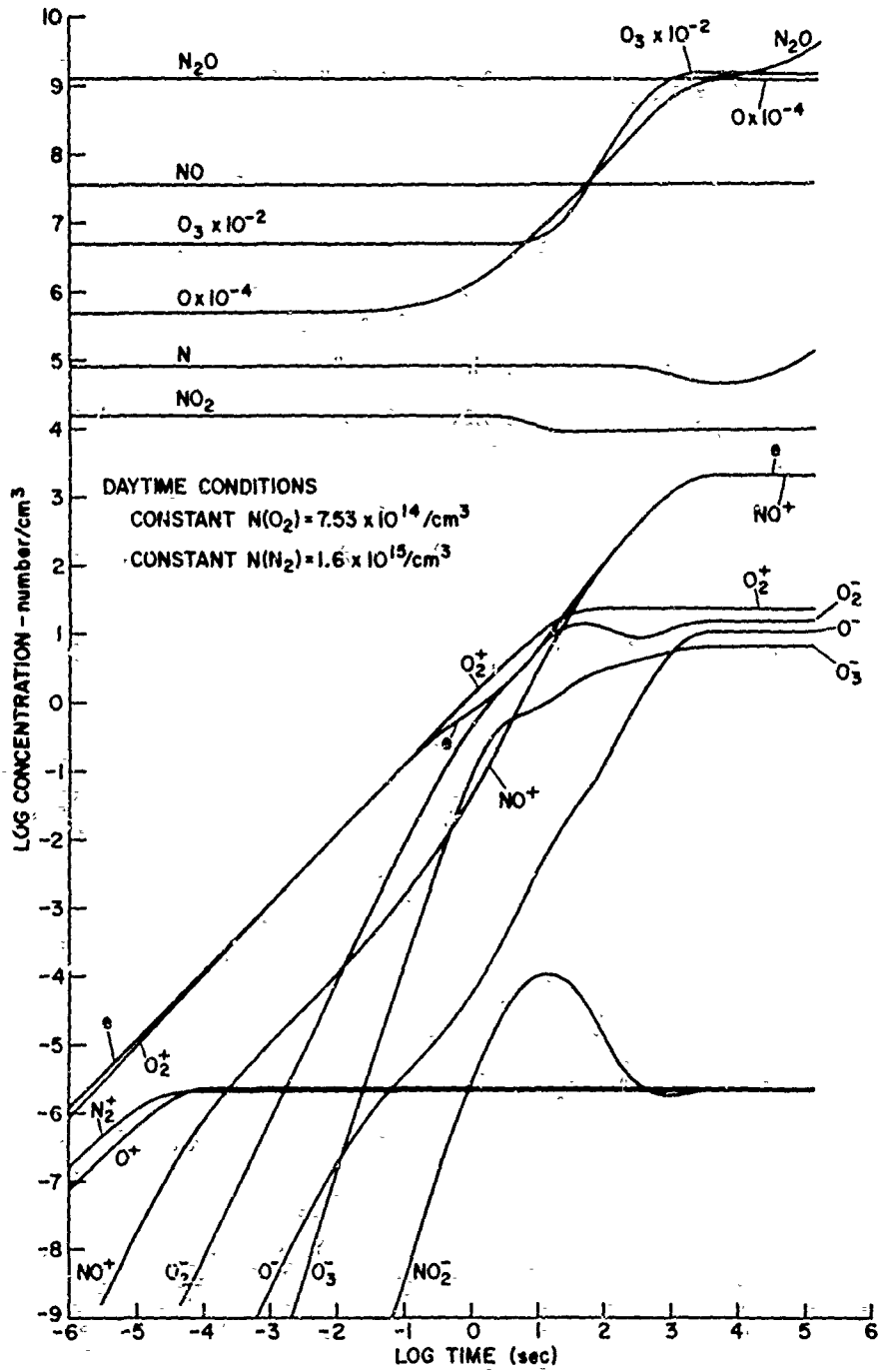


Figure 1. Solution at 70 km with Zero-Initial Conditions on the Charged Species and a Constant Source of 1.122 ion-pairs/ $\text{cm}^3/\text{sec}$

$O + O_2 + M \longrightarrow O_3 + M$  is about  $3 \times 10^3$  secs. After this time, the formation rate by photodissociation and the removal rate by recombination become equal, causing the atomic oxygen concentration to go into equilibrium.

The ozone concentration cannot change until enough of these molecules are formed by the three-body recombination reaction  $O + O_2 + M \longrightarrow O_3 + M$  to start increasing the number present. They are removed by photodissociation with a time constant of about 100 secs. After this time, the recombination rate equals the photodissociation rate causing the ozone concentration to level off at a value established by the equilibrium concentration of atomic oxygen.

The time constants for the removal of  $N_2O$  are all greater than  $10^5$  secs. However, by  $10^4$  secs, the two-body atomic recombination reaction  $O + N_2 \longrightarrow N_2O + h\nu$  has formed a sufficient number of these molecules to start increasing its concentration. Its density increases by this process and continues to do so until the removal processes become effective after  $10^5$  secs.

The time constant for the removal of nitric oxide by the three-body recombination reaction  $O + NO + M \longrightarrow NO_2 + M$  is about  $10^4$  secs. Before any  $NO$  molecules can be removed, however, their production by the neutral rearrangement reaction  $O + NO_2 \longrightarrow NO + O_2$  becomes effective. Around  $10^4$  secs the rates of these two processes become equal which is the reason for there being no change in the  $NO$  concentration. The atomic nitrogen concentration remains constant until about 100 secs, the time constant for the removal process  $N + O \longrightarrow NO + h\nu$ , when its concentration starts to decrease. When the rate of this removal reaction becomes equal to the rate of formation of atomic nitrogen by the photodissociation of  $N_2O$ , the  $N$  concentration goes into quasi-equilibrium with  $N_2O$ .

There is no effective removal process for  $NO_2$  molecules at early times. The time constant for their removal by the neutral rearrangement reaction  $O + NO_2 \longrightarrow NO + O_2$  is about 2 secs. By 10 secs, however, their rate of production by the three-body recombination  $O + NO + M \longrightarrow NO_2 + M$  is sufficient to balance their removal rate thus preventing any further change in their concentration.

The electron density increases with unit slope at early times as electrons are formed by the constant source. By 0.1 sec, 0.1122 electrons are produced. During this time, the  $O_2^-$  concentration increases with slope 2 as this ion is formed by the three-body attachment reaction  $O_2 + e + O_2 \longrightarrow O_2^- + O_2$ . The time constant for the removal of electrons by this three-body attachment is about 0.8 sec. It was expected that  $O_2^-$  photodetachment become effective around this time, causing a balance between the attachment and detachment and putting the  $O_2^-$  density into quasi-equilibrium with the electron density. This quasi-equilibrium effect is clearly seen in Figure 7 of Keneshea (1963). The time constant for photodetachment is about 2 secs, however, so that the production of  $O_2^-$  by attachment continues, causing the electron density to decrease. Another important removal process for

$O_2^-$  ions is the charge transfer reaction  $O_2^- + O_3 \rightarrow O_3^- + O_2$ . Because of the increasing  $O_3$  density after 10 secs, it is not possible to fix a definite time constant to this reaction. The final equilibrium between the electrons and the  $O_2^-$  ions is determined by the ozone equilibrium concentration. This behavior can be understood if the  $O_2^-$  to electron ratio is determined from equilibrium considerations. The  $O_2^-$  differential equation at equilibrium is essentially

$$\frac{dN(O_2^-)}{dt} = -N(O_2^-) \left[ N(O_3) \cdot k_{96} + k_1 \right] + N(O_2)^2 \cdot N(e) \cdot k_{24} = 0 \quad (4)$$

From Eq. (4), the ratio of  $O_2^-$  to electrons is

$$\frac{N(O_2^-)}{N(e)} = \frac{N(O_2)^2 \cdot k_{24}}{N(O_3) \cdot k_{96} + k_1} \quad (5)$$

It is obvious that this ratio depends only on the ozone concentration. After 100 secs, the electron concentration returns to a linear increase resulting from the production by the source and goes into equilibrium when the rate of production by the source equals the rate of removal by dissociative recombination with  $NO^+$ .

The  $O^-$  concentration increases at early times with a slope of 2 as this ion is formed by the dissociative attachment reaction  $O_3 + e \rightarrow O^- + O_2$ . The time constant for the associative detachment reaction  $O^- + N_2 \rightarrow N_2O + e$  is about  $6 \times 10^{-3}$  secs around which time removal of this ion becomes effective. As the concentration of  $O_2^-$  increases, the charge transfer reaction  $O_2^- + O \rightarrow O^- + O_2$  eventually becomes effective in forming  $O^-$  ions. Around 1 sec, the density of this ion goes into quasi-equilibrium with the electrons and  $O_2^-$  as the rate of formation by the dissociative attachment and the charge transfer equals the removal rate of the associative detachment. Because of its quasi-equilibrium status, the  $O^-$  concentration continues to increase after 1 sec. Around 100 secs, the concentrations of ozone and  $O^-$  have reached values that make the removal of this ion by the charge transfer reaction  $O^- + O_3 \rightarrow O_3^- + O$  become important. The final equilibrium level of  $O^-$  and its ratio to the electron density are determined by the equilibrium value of ozone.

At early times, the  $O_3^-$  concentration increases with a slope of 3 being formed by the charge transfer reaction  $O_2^- + O_3 \rightarrow O_3^- + O_2$ . Before the  $O^-$  density changes, the time constant for the removal of this ion by the associative detachment reaction  $O_3^- + O \rightarrow 2O_2 + e$  is about 2 secs. As the concentration of atomic oxygen increases, this time constant becomes smaller. When both atomic oxygen and ozone reach equilibrium values, the  $O_3^-$  concentration goes into equilibrium at a ratio to the  $O_2^-$  density that is established by the atomic oxygen and the ozone concentrations.

The  $\text{NO}_2^-$  concentration increases at early times with a slope of 3 since it is formed by the charge transfer reaction  $\text{O}_2^- + \text{NO}_2 \longrightarrow \text{NO}_2^- + \text{O}_2$ . As long as the ozone concentration is constant, the time constant for the removal of this ion by the charge transfer reaction  $\text{NO}_2^- + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_3^-$  is about 2 secs. This is the same time that the ozone concentration starts to increase, causing the rate of the charge transfer to  $\text{O}_3^-$  to become much larger than the rate of the charge transfer to  $\text{NO}_2^-$ . This causes the  $\text{NO}_2^-$  concentration to decay. This decay continues until the ozone concentration reaches a constant value, causing the  $\text{NO}_2^-$  density to go into equilibrium at a fixed ratio to the  $\text{O}_2^-$  density.

The concentrations of both  $\text{O}^+$  and  $\text{N}_2^+$  increase linearly at early times as these ions are formed by the constant source. The time constant for the removal of  $\text{O}^+$  ions by the charge transfer reaction  $\text{O}^+ + \text{O}_2 \longrightarrow \text{O}_2^+ + \text{O}$  is about  $3 \times 10^{-5}$  secs while the time constant for the removal of  $\text{N}_2^+$  ions by the charge transfer reaction  $\text{N}_2^+ + \text{O}_2 \longrightarrow \text{O}_2^+ + \text{N}_2$  is about  $1 \times 10^{-5}$  secs. Around these times, therefore, the charge transfer rates become equal to the rates of production of these ions by the source and their concentrations go into equilibrium. All  $\text{O}^+$  and  $\text{N}_2^+$  ions produced by the source after this time immediately transfer their charge to form  $\text{O}_2^+$  ions.

The  $\text{O}_2^+$  concentration increases at early times because of the production by the constant source and the transfer of charge from the  $\text{N}_2^+$  ions as the latter are formed by the constant source. The charged rearrangement reaction  $\text{O}_2^+ + \text{N}_2 \longrightarrow \text{NO}^+ + \text{NO}$  has a time constant of about 50 secs. After this time, the  $\text{O}_2^+$  goes into equilibrium at a value that is determined by the balance between the source function and the charged rearrangement reaction.

The  $\text{NO}^+$  concentration builds up with a slope of 2 at very early times through its formation by the charged rearrangement reaction  $\text{O}^+ + \text{N}_2 \longrightarrow \text{NO}^+ + \text{N}$ . When  $\text{O}^+$  goes into equilibrium, the slope of the  $\text{NO}^+$  profile changes to 1. By 0.1 sec, enough  $\text{O}_2^+$  ions are formed to make the charge transfer process  $\text{O}_2^+ + \text{NO} \longrightarrow \text{NO}^+ + \text{O}_2$  become more important in the formation of  $\text{NO}^+$  ions, causing the slope to change back to 2. When  $\text{O}_2^+$  goes into equilibrium, the  $\text{NO}^+$  concentration reverts to unit slope increase. The time constant for dissociative recombination is about  $10^3$  secs after which time the production rate of  $\text{NO}^+$  by charge transfer from  $\text{O}_2^+$  equals the removal rate, causing the  $\text{NO}^+$  concentration to go into equilibrium.

Figure 2 shows the solution at 110 km with zero initial concentrations of the ionized species and estimated initial concentrations of the minor neutral species. There is a continuing constant source producing ion-pairs at the rate of  $2 \times 10^3/\text{cm}^3/\text{sec}$ .

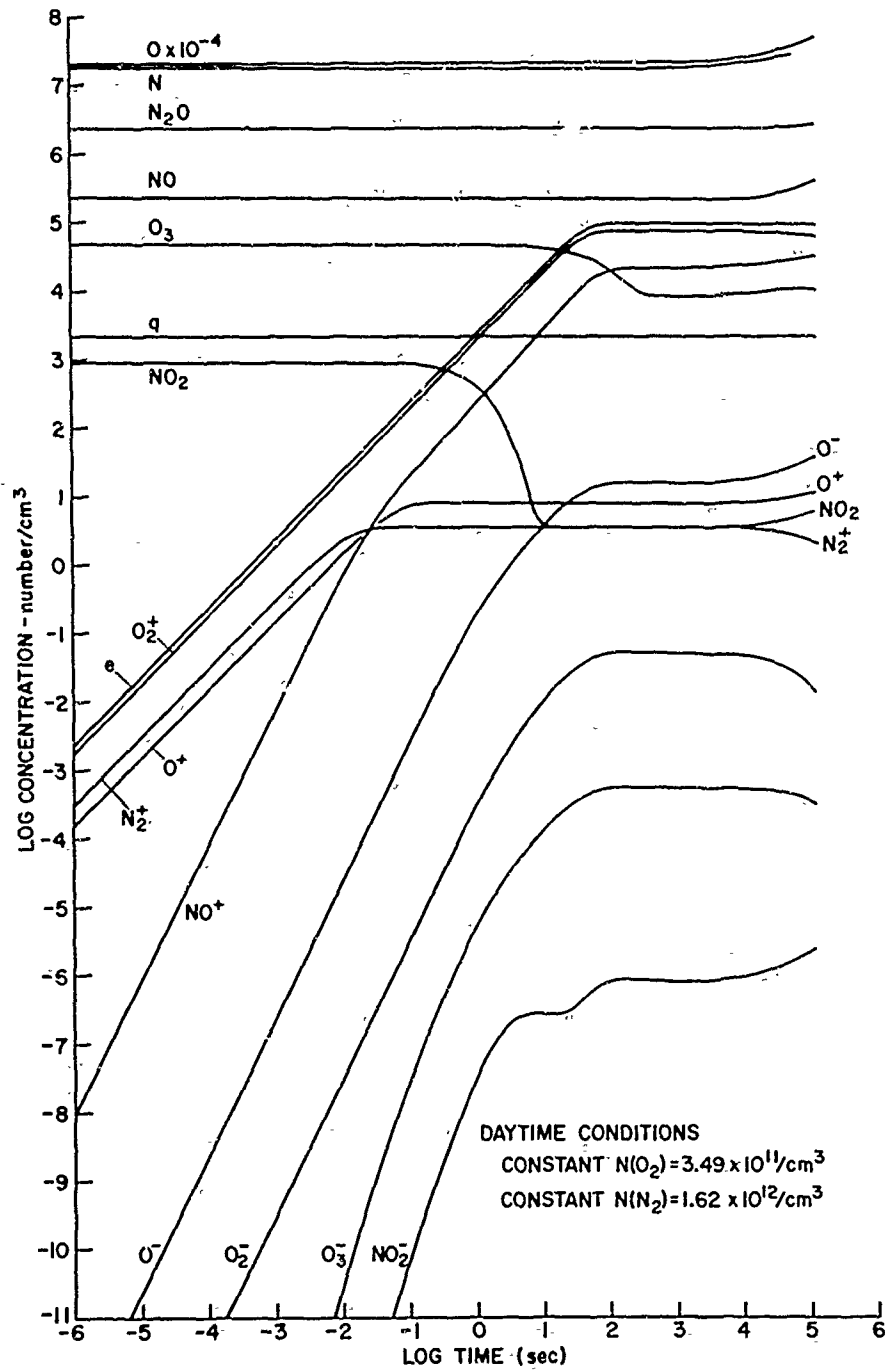


Figure 2. Solution at 110 km with Zero Initial Conditions on the Charged Species and a Constant Source of  $2 \times 10^3$  ion-pairs/cm<sup>3</sup>/sec



The time constants of the processes that remove atomic oxygen are greater than  $10^5$  secs. The increase in the density of this atom at late times results from the photodissociation of  $O_2$ . The time constants of the processes that remove N, NO, and  $N_2O$  are all greater than  $10^5$  secs. The atomic nitrogen concentration increases at late times because the dissociative recombination of  $NO^+$  has started to form a sufficient number of these atoms to start increasing their concentration. The associative detachment reaction  $O^- + N_2 \rightarrow N_2O + e$  has formed about  $10^6$   $N_2O$  molecules in  $10^5$  secs which accounts for the slight increase in their concentration at very late times. The increase in the NO density at late times results from the increasing N and O concentrations in the two-body atom recombination reaction  $N + O \rightarrow NO + h\nu$ .

The ozone concentration remains constant until about 100 secs when  $O_3$  starts to be removed by photodissociation. The time constant for the two-body atom recombination reaction  $O + O_2 \rightarrow O_3 + h\nu$  is about 600 secs. After this time, the ozone concentration goes into equilibrium which is established by the atomic-oxygen concentration. The increase in  $O_3$  at late times is caused by the increasing oxygen supply for the two-body atom recombination reaction. The time constant for the neutral rearrangement reaction  $O + NO_2 \rightarrow NO + O_2$  is about 1 sec. After this time, the  $NO_2$  concentration decays until the rate of removal is reduced to the rate of formation by the two-body atom recombination reaction  $O + NO \rightarrow NO_2 + h\nu$  when the  $NO_2$  concentration remains at the equilibrium value established by these reactions.

The electron concentration increases at early times with unit slope as they are formed by the constant source. By 1 sec,  $2 \times 10^3$  electrons are formed. The time constant for the  $O_2^+$  dissociative recombination is about 50 secs around which time the rate of production by the source and the rate of removal by dissociative recombination become equal and the electron concentration goes into equilibrium. The most important formation process for  $O^-$  ions is the radiative attachment reaction  $O + e \rightarrow O^- + h\nu$ . The  $O^-$  concentration increases with a slope of 2 as this ion is formed by this process. The time constant for  $O^-$  photodetachment is about 0.75 sec when their removal starts to become effective and they assume a constant ratio to the electrons. The increase in the  $O^-$  concentration at late times reflects the dependence of the equilibrium value of this ion on the atomic-oxygen concentration.

At early times, the  $O_2^-$  concentration increases with a slope of 2 as it is formed by the three-body attachment reaction  $O_2 + e + M \rightarrow O_2^- + M$ . There are two important removal processes for this ion both with time constants of about 2 secs. These are the photodetachment and the charge transfer reaction  $O_2^- + O \rightarrow O^- + O_2$ . Around this time  $O_2^-$  goes into quasi-equilibrium with the

electrons and assumes a fixed ratio to them. At very late times, the increasing atomic-oxygen concentration increases the rate of removal of  $O_2^-$  by the charge transfer, causing the  $O_2^-$  concentration to decrease and thereby change the ratio established between  $O_2^-$  and the electrons.

The  $O_3^-$  ions are formed primarily by the two-body ion-neutral association reaction  $O^- + O_2 \rightarrow O_3^- + h\nu$ . The  $O_3^-$  density increases with a slope of 3 at early times as they are formed by this process. The time constant for the associative detachment reaction  $O_3^- + O \rightarrow O_2 + e + O_2$  is about 0.1 sec after which time it becomes effective in removing  $O_3^-$  ions and causes their concentration to remain at a constant ratio to the electrons. This ratio is no longer constant after  $10^4$  secs because the rate of the associative detachment reaction increases with the increasing atomic-oxygen concentration.

The  $NO_2^-$  concentration increases with a slope of 3 at early times as it is formed by the charge transfer reaction  $O^- + NO_2 \rightarrow NO_2^- + O$ . Changes in slope are dictated by the  $O^-$  and  $NO_2$  curves. The time constant for  $NO_2^-$  photo-detachment is about 25 secs after which time quasi-equilibrium with  $O^-$  is established.

The  $O^+$  and  $N_2^+$  concentrations increase with unit slope at early times through their formation by the constant source. The time constant for the charge transfer reaction  $O^+ + O_2 \rightarrow O_2^+ + O$  is about 0.07 sec. After this time, the removal of  $O^+$  ions becomes effective and quickly equalizes the production by the source forcing the  $O^+$  concentration into equilibrium. Removal of  $N_2^+$  ions starts around 0.02 sec which is the time constant for their removal by the charged rearrangement reaction  $N_2^+ + O \rightarrow NO^+ + N$ . The equilibrium value of  $N_2^+$  is the result of the balance achieved between the source and the charged rearrangement. The decay of  $N_2^+$  after  $10^4$  secs is simply the result of the increasing rate of the charged rearrangement reaction resulting from the increasing atomic-oxygen concentration. Any further production of  $O^+$  and  $N_2^+$  ions by the source after they have gone into equilibrium is immediately transferred into  $O_2^+$  ions.

The  $O_2^+$  concentration increases with unit slope until about 50 secs when dissociative recombination starts to remove them. By 100 secs, the  $O_2^+$  concentration reaches an equilibrium determined by the source and the dissociative recombination. At late times, the charged rearrangement reaction  $O_2^+ + N \rightarrow NO^+ + O$  becomes important to the equilibrium of  $O_2^+$ . The decrease in  $O_2^+$  after  $10^4$  secs is caused by the increased rate of this reaction as the density of atomic nitrogen increases. The major source of  $NO^+$  ions at early times is the charged rearrangement reaction  $N_2^+ + O \rightarrow NO^+ + N$ . The  $NO^+$  concentration increases with a slope of 2 until  $N_2^+$  goes into equilibrium at which time the slope of the  $NO^+$  profile changes to unity. Around 50 secs, the charged rearrangement reaction

$O_2^+ + N \rightarrow NO^+ + O$  becomes the important formation process for  $NO^+$  ions. This is also the time that the dissociative recombination becomes effective in removing these ions. The equilibrium value of  $NO^+$  is determined by the balance between the charged rearrangement reaction and the dissociative recombination. The increase in the  $NO^+$  concentration at late times results from the increased production by the charged rearrangement reaction as the atomic-nitrogen density increases.

Figure 3 shows the solution at 70 km assuming high initial concentrations, such as during a nuclear blackout, for the electrons,  $O^+$ ,  $O_2^+$ , and  $N_2^+$ , zero concentrations of the other charged species and estimated initial concentrations for the minor neutral species. A small continuing source of 0.1 ion-pairs/cm<sup>3</sup>/sec is used. The time constant for dissociative recombination is very short (about 0.2 sec) because of the high initial concentrations of electrons and  $O_2^+$  ions. The electrons remain constant until this time and they start to decay by dissociative recombination with  $O_2^+$  and three-body attachment to  $O_2$ .

The  $O_2^-$  concentration increases linearly from early times by the three-body attachment reaction  $O_2 + e + O_2 \rightarrow O_2^- + O_2$ . This increase continues until about 1 sec which is the time constant for  $O_2^-$  photodetachment. The charge-transfer reactions  $O_2^- + O \rightarrow O^- + O_2$  and  $O_2^- + O_3 \rightarrow O_3^- + O_2$  also become effective in removing  $O_2^-$  after 1 sec. By 50 sec, the  $O_2^-$  concentration has gone into quasi-equilibrium with the electrons, O, and  $O_3$ . The behavior of the negative ions after they have gone into quasi-equilibrium can be understood by looking at their equilibrium equations. The differential equation for  $O_2^-$  in equilibrium can be written as

$$\begin{aligned} \frac{dN(O_2^-)}{dt} = & -N(O_2^-) \cdot [k_1 + N(O) \cdot k_{94} + N(O_3) \cdot k_{96}] \\ & + N^2(O_2) \cdot N(e) \cdot k_{24} = 0 \end{aligned} \quad (6)$$

Solving Eq. (6) for the ratio  $N(O_2^-)/N(e)$  gives

$$\frac{N(O_2^-)}{N(e)} = \frac{N^2(O_2) \cdot k_{24}}{(k_1 + N(O) \cdot k_{94} + N(O_3) \cdot k_{96})} \quad (7)$$

As long as the O and  $O_3$  concentrations are increasing, this ratio becomes smaller and smaller assuming a constant value only when O and  $O_3$  go into equilibrium.

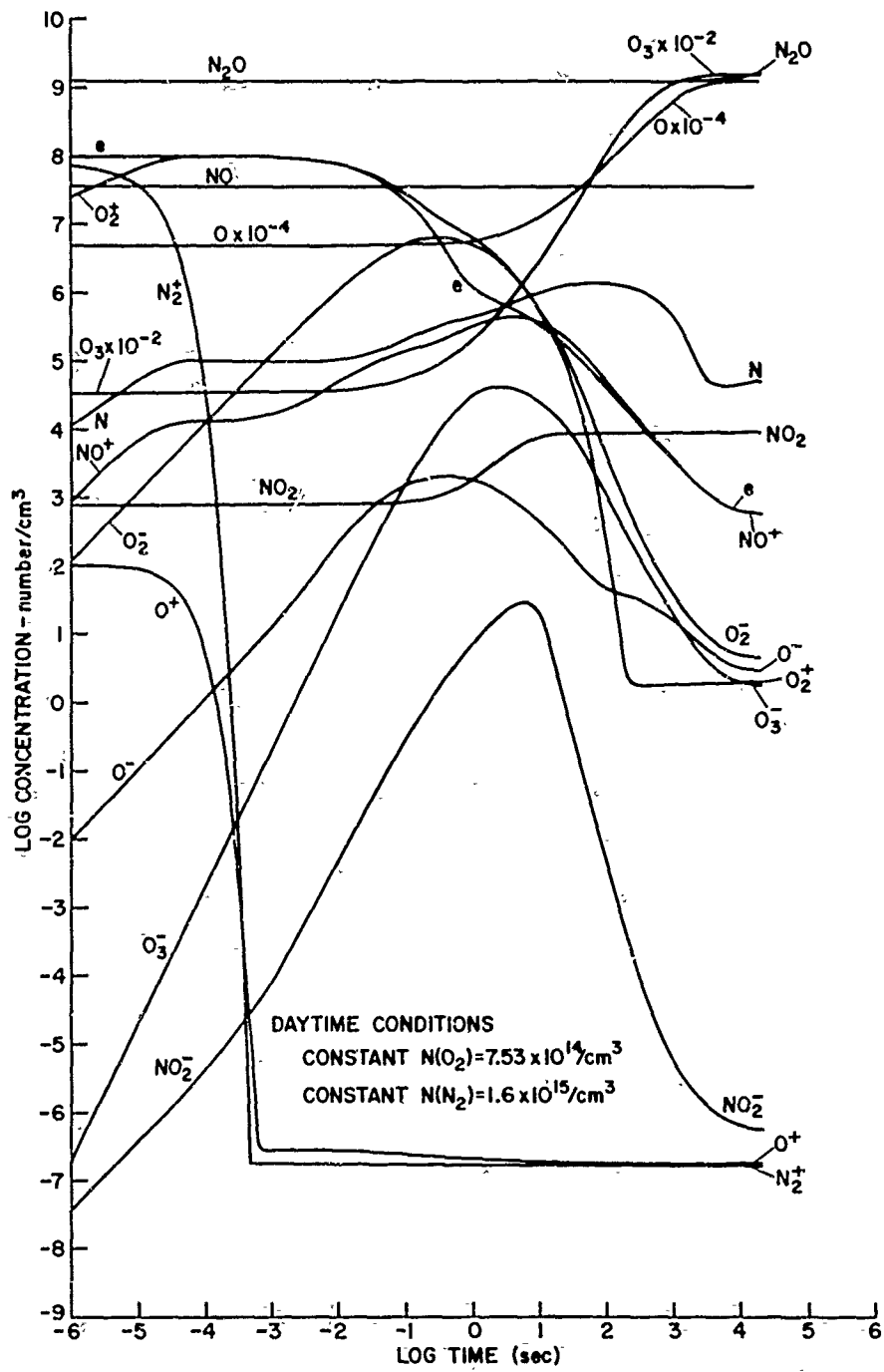


Figure 3. Solution at 70 km with High Initial Electron Concentration

The  $O^-$  concentration increases with unit slope at early times as this ion is formed by the associative detachment reaction  $O_3 + e \rightarrow O^- + O_2$ . The formation of  $O^-$  ions by the charge transfer reaction  $O_2^- + O \rightarrow O^- + O_2$  becomes effective around  $10^{-3}$  secs. The time constant for removal of  $O^-$  ions by the associative detachment reaction  $O^- + N_2 \rightarrow N_2O + e$  is about  $10^{-2}$  secs. This reaction starts to consume this ion after this time and by 1 sec the  $O^-$  concentration goes into quasi-equilibrium with the electrons,  $O_2^-$ ,  $O$ , and  $O_3$ . The differential equation for  $O^-$  at equilibrium is

$$\begin{aligned} \frac{dN(O^-)}{dt} = & -N(O^-) \cdot \left[ N(N_2) \cdot k_{11} + N(O_3) \cdot k_{93} \right] + N(O_3) \cdot N(e) \cdot k_{20} \\ & + N(O_2^-) \cdot N(O) \cdot k_{24} = 0 \end{aligned} \quad (8)$$

Solving Eq. (8) for the ratio  $N(O^-)/N(e)$  gives

$$\frac{N(O^-)}{N(e)} = \frac{N(O_3) \cdot k_{20} + \frac{N(O_2^-)}{N(e)} \cdot N(O) \cdot k_{94}}{N(N_2) \cdot k_{11} + N(O_3) \cdot k_{93}} \quad (9)$$

The ratio  $N(O^-)/N(e)$  is not a simple one but it is obvious that it depends only upon the  $O$  and  $O_3$  concentrations and becomes constant only when  $O$  and  $O_3$  go into equilibrium.

The  $O_3^-$  concentration increases with a slope of 2 at the beginning as this ion is formed by the charge transfer reaction  $O_2^- + O_3 \rightarrow O_3^- + O_2$ . The time constant for the associative detachment reaction  $O_3^- + O \rightarrow 2O_2 + e$  is about 1 sec. Shortly after this time, the detachment rate becomes equal to the charge transfer rate, causing the  $O_3^-$  concentration to go into quasi-equilibrium with the electrons,  $O$ , and  $O_3$ . The differential equation for  $O_3^-$  at equilibrium can be written as

$$\frac{dN(O_3^-)}{dt} = -N(O_3^-) \cdot N(O) \cdot k_{167} + N(O_2^-) \cdot N(O_3) \cdot k_{96} = 0 \quad (10)$$

Solving Eq. (10) for the ratio  $N(O_3^-)/N(e)$  gives

$$\frac{N(O_3^-)}{N(e)} = \frac{N(O_3) \cdot k_{96} \cdot N^2(O_2) \cdot k_{24}}{N(O) \cdot k_{167} [K_1 + N(O) \cdot k_{94} + N(O_3) \cdot k_{96}]} \quad (11)$$

This ratio depends only upon the concentration of  $O$  and  $O_3$  and becomes constant when  $O$  and  $O_3$  go into equilibrium.

The  $\text{NO}_2^-$  ions are formed at early times by the three-body attachment reaction  $\text{NO}_2 + e + \text{O}_2 \rightarrow \text{NO}_2^- + \text{O}_2$ . By  $10^{-3}$  secs, there are enough  $\text{O}_2^-$  ions around to make the charge transfer reaction  $\text{O}_2^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{O}_2$  more important in forming  $\text{NO}_2^-$  ions accounting for the change of slope to 2. The time constant for the charge transfer reaction  $\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_3^-$  is about 3 secs. Shortly after this time the  $\text{NO}_2^-$  concentration goes into quasi-equilibrium with  $\text{O}_3^-$ ,  $\text{O}_2^-$ , and  $\text{O}_3$ . The differential equation for  $\text{NO}_2^-$  at equilibrium is

$$\begin{aligned} \frac{dN(\text{NO}_2^-)}{dt} &= -N(\text{NO}_2^-) \cdot N(\text{O}_3) \cdot k_{97} + N(\text{O}_3^-) \cdot N(\text{NO}_2) \cdot k_{98} \\ &+ N(\text{O}_2^-) \cdot N(\text{NO}_2) \cdot k_{95} = 0 \end{aligned} \quad (12)$$

Solving Eq. (12) for the ratio  $N(\text{NO}_2^-)/N(\text{O}_2^-)$  gives

$$\frac{N(\text{NO}_2^-)}{N(\text{O}_2^-)} = \frac{\frac{N(\text{O}_3^-)}{N(\text{O}_2^-)} \cdot N(\text{NO}_2) \cdot k_{98} + N(\text{NO}_2) \cdot k_{95}}{N(\text{O}_3) \cdot k_{97}} \quad (13)$$

From Eq. (13) it is obvious that the ratio  $N(\text{NO}_2^-)/N(\text{O}_2^-)$  is solely a function of  $\text{NO}_2$ ,  $\text{O}$ , and  $\text{O}_3$  and that this ratio becomes constant only when  $\text{NO}_2$ ,  $\text{O}$ , and  $\text{O}_3$  go into equilibrium.

The  $\text{O}^+$  and  $\text{N}_2^+$  concentrations decay at early times by charge transfer to  $\text{O}_2$ . The concentrations of both of these ions continues to decay until the rate of removal is reduced to the small rate of production by the source function and they go into equilibrium. The  $\text{O}_2^+$  concentration increases at very early times as these ions are formed by charge transfer from  $\text{N}_2^+$ . This increase stops when the  $\text{N}_2^+$  is effectively consumed. The time constant for  $\text{O}_2^+$  dissociative recombination is about 0.2 sec around which time these ions start to be removed. The mutual neutralization reaction  $\text{O}_2^- + \text{O}_2^+ \rightarrow \text{O}_2 + \text{O}_2$  and the charge transfer reaction  $\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$  both have time constants of about 2 secs when they become effective in removing the  $\text{O}_2^+$  ions. These processes continue to remove  $\text{O}_2^+$  until its concentration goes into equilibrium when the rates of removal equal the small rate of production by the constant source.

$\text{NO}^+$  ions are formed at early times by the charge transfer reaction  $\text{N}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2$ . When the supply of  $\text{N}_2^+$  is used up,  $\text{NO}^+$  is formed at about equal rates by the charge transfer reaction  $\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$  and the charged rearrangement reaction  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$ . The time constant for  $\text{NO}^+$  dissociative recombination is about 0.1 sec around which time removal of  $\text{NO}^+$  becomes effective. At about 3 secs removal and production of  $\text{NO}^+$  become equal. The production of  $\text{NO}^+$  becomes constant around 200 secs when  $\text{O}_2^+$  goes into equilibrium.

After this time the  $\text{NO}^+$  concentration decays by dissociative recombination along with the electron concentration until the removal rate by recombination equals the production rate from  $\text{O}_2^+$  and the  $\text{NO}^+$  concentration goes into equilibrium.

The atomic nitrogen concentration increases at early times as a product of the charged rearrangement reaction  $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$ . When  $\text{N}_2^+$  has decayed away this production of N atoms stops. By  $10^{-2}$  secs, enough N atoms are formed as a product of the  $\text{NO}^+$  dissociative recombination to start increasing the N concentration. The neutral rearrangement reaction  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$  has a time constant of about  $10^3$  secs. Around this time, the production of N atoms by dissociative recombination has slowed down because of the decaying  $\text{NO}^+$  concentration allowing these atoms to be consumed by the neutral rearrangement. At very late times,  $\text{NO}^+$  dissociative recombination ceases to be the important formation mechanism for N atoms because of the relatively low  $\text{NO}^+$  concentration. The important formation process for N atoms becomes the photodissociation of  $\text{N}_2\text{O}$  which has formed about  $5 \times 10^4$  atoms in  $10^4$  secs. The atomic nitrogen concentration after  $10^4$  secs, therefore, is determined by the neutral rearrangement and the photodissociation.

The time constant for the removal of  $\text{NO}_2$  by the neutral rearrangement reaction  $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$  is about 5 secs. The  $\text{NO}_2$  concentration remains constant up to about 0.1 sec by which time the three-body atom recombination reaction  $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$  has formed about  $10^2$  of these molecules. This is sufficient for the  $\text{NO}_2$  concentration to show an increase. By 10 secs, the neutral rearrangement balances the three-body atom recombination forcing the  $\text{NO}_2$  concentration into equilibrium. The fact that O is involved both in the production and removal processes makes  $\text{NO}_2$  independent of O.

The behavior of  $\text{N}_2\text{O}$ ,  $\text{O}_3$ , and atomic oxygen are essentially the same as shown in Figure 1.

Figure 4 shows the behavior at 110 km of initial high ionization and a very small continuing source. Initially there are  $10^8$  electrons/cm<sup>3</sup> with equal positive ionization partitioned among  $\text{O}^+$ ,  $\text{O}_2^+$ , and  $\text{N}_2^+$  according to the relative amounts of the corresponding neutral species present. The negative ions and  $\text{NO}^+$  have zero initial concentrations while the minor neutral species start out at estimated initial concentrations. For convenience, a small constant source of 0.1 ion-pairs/cm<sup>3</sup>/sec is used.

The time constant for  $\text{O}_2^+$  and  $\text{NO}^+$  dissociative recombination is about 0.25 sec because of the high ion and electron concentrations. The electron density remains constant until about 0.25 sec, therefore, and decays by the simple recombination law after this time. Around  $10^4$  secs, the rate of removal of electrons by recombination equals the rate of formation by the small continuing source, causing the electron concentration to go into equilibrium. The  $\text{O}_2^+$  concentration remains

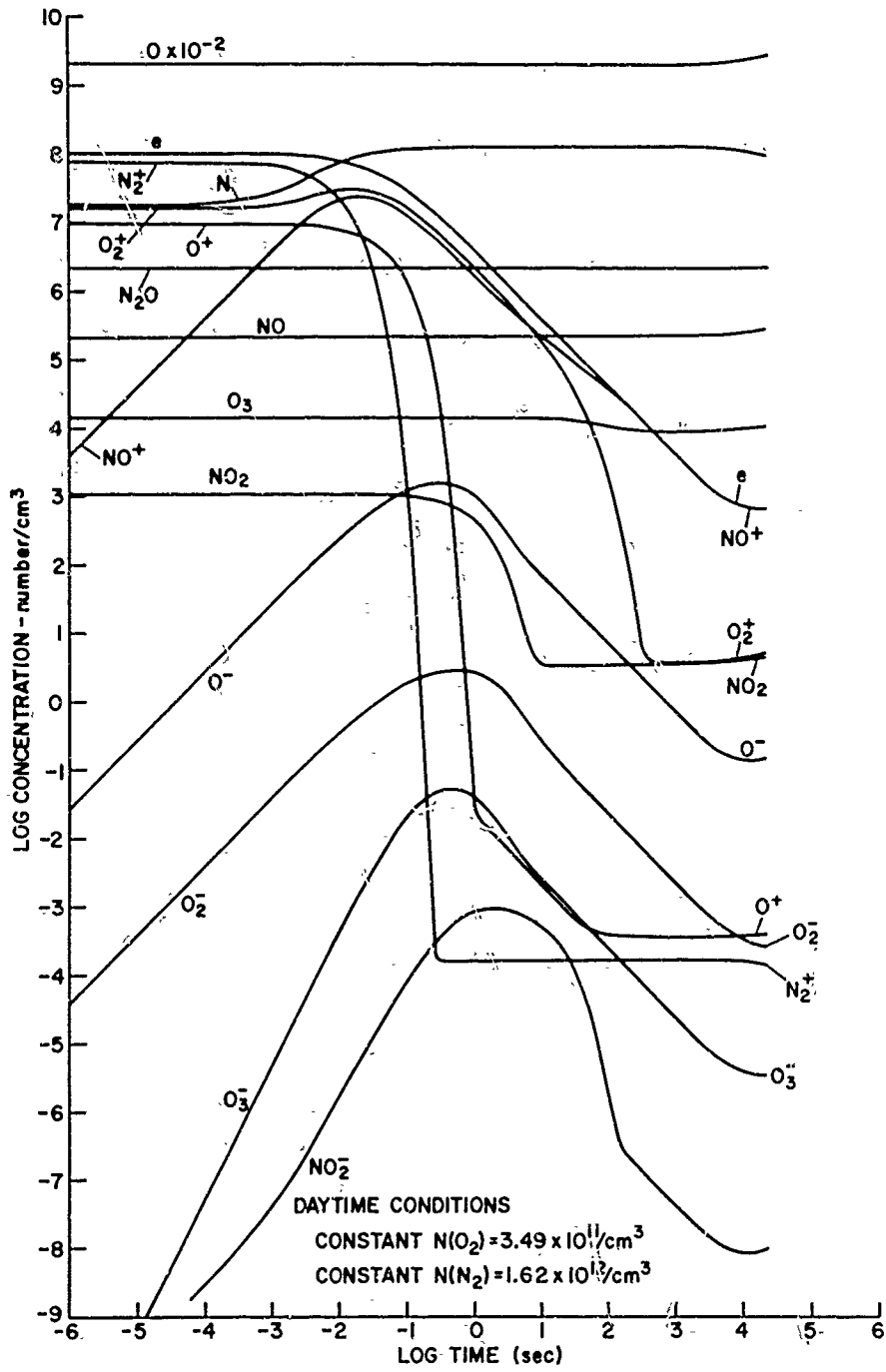


Figure 4. Solution at 110 km with High Initial Electron Concentrations



constant at early times with a slight increase around  $10^{-2}$  secs because of the increased production rate of the charge transfer reaction  $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ . Around 0.25 sec, dissociative recombination becomes effective in removing this ion, causing it to go into a recombination-type decay. By 50 secs, however, the time constant for  $O_2^+$  dissociative recombination has become rather long because of the much lower electron concentration at this time. The time constant for the charged rearrangement reaction  $O_2^+ + N \rightarrow NO^+ + O$  is about 50 secs. Around this time, therefore, the removal of  $O_2^+$  is accomplished by the charged rearrangement which has become faster than the dissociative recombination. The  $O_2^+$  concentration goes into equilibrium when the rate of removal by charged rearrangement equals the rate of formation by the small constant source. The  $NO^+$  concentration increases with unit slope at the start of the solution as this ion is formed by the charged rearrangement reaction  $N_2^+ + O \rightarrow NO^+ + N$ . This increase continues until about 0.25 sec which is the time constant for  $NO^+$  dissociative recombination. After this time, the  $NO^+$  concentration decays by the simple recombination law. Around 10 secs, the production of  $NO^+$  by the charged rearrangement reaction  $O_2^+ + N \rightarrow NO^+ + O$  becomes effective. When the  $O_2^+$  density is sufficiently reduced, the charged rearrangement reaction becomes ineffectual and the  $NO^+$  decay returns to the recombination law.

The time constant for the removal of  $O^+$  ions by the charge transfer reaction  $O^+ + O_2 \rightarrow O_2^+ + O$  is about 0.07 sec around which time the  $O^+$  concentration starts to decay. This removal continues until about 1 sec when the charged rearrangement reaction  $O_2^+ + N \rightarrow O^+ + NO$  becomes effective in forming this ion and around 7 secs the  $O^+$  concentration goes into quasi-equilibrium. The differential equation for  $O^+$  at equilibrium can be written as

$$\frac{dN(O^+)}{dt} = -N(O^+) \cdot \left[ N(O_2) \cdot k_{83} + N(N_2) \cdot k_{116} \right] + N(O_2^+) \cdot N(N) \cdot k_{118} + q = 0. \quad (14)$$

Solving Eq. (14) for  $N(O^+)$  gives

$$N(O^+) = \frac{q + N(O_2^+) \cdot N(N) \cdot k_{118}}{N(O_2) \cdot k_{83} + N(N_2) \cdot k_{116}} \quad (15)$$

From this result it is obvious that the variation in the  $O^+$  concentration must follow the variation in the  $O_2^+$  concentration. This is the reason for the linear decrease around 10 secs. When the rate of the charged rearrangement  $O_2^+ + N \rightarrow O^+ + NO$  becomes smaller than the production rate of the continuing source, the  $O^+$  density becomes constant.

The time constant for the removal of  $N_2^+$  by the charged rearrangement reaction  $N_2^+ + O \rightarrow NO^+ + N$  and the charge transfer reaction  $N_2^+ + O_2 \rightarrow O_2^+ + N_2$  is about 0.02 sec. The  $N_2^+$  concentration decays after this time until the rate of removal equals the rate of formation by the continuing source and the  $N_2^+$  concentration goes into equilibrium.

The  $O^-$  concentration increases with unit slope at the beginning of the solution as this ion is formed by the radiative attachment reaction  $O + e \rightarrow O^- + h\nu$ . The time constant for photodetachment from  $O^-$  is about 0.75 sec around which time the detachment rate exceeds the attachment rate, causing the  $O^-$  concentration to decay. The density of  $O^-$  does not go into quasi-equilibrium with the electrons until about 70 secs. After this time, the  $O^-$  density assumes a constant ratio to the electron density. The  $O_2^-$  concentration also increases with unit slope at early times as this ion is formed by the three-body attachment reaction  $O_2 + e + M \rightarrow O_2^- + M$ . Around 1 sec, the time constant for photodetachment from  $O_2^-$  and the charge transfer reaction  $O_2^- + O \rightarrow O^- + O_2$ , the removal rate exceeds the formation rate, causing  $O_2^-$  to decay. Around 100 secs the  $O_2^-$  concentration goes into quasi-equilibrium with the electrons and after this time it varies at a fixed ratio to the electron concentration.

The  $O_3^-$  concentration increases with a slope of 2 at the start because of the formation of this ion by the ion-neutral association reaction  $O^- + O_2 \rightarrow O_3^- + h\nu$ . The associative detachment reaction  $O_3^- + O \rightarrow 2O_2 + e$  has a time constant of about 0.1 sec after which it exceeds the rate of attachment, causing the  $O_3^-$  to decay. The  $O_3^-$  goes into quasi-equilibrium around 5 secs and assumes a fixed ratio to the electron concentration. The  $NO_2^-$  ions are formed at early times by the three-body attachment reaction  $NO_2 + e + M \rightarrow NO_2^- + M$ . The  $NO_2^-$  concentration increases with unit slope, therefore, before  $10^{-4}$  secs. As the  $O^-$  concentration increases, the  $NO_2^-$  production process changes to the charge transfer reaction  $O^- + NO_2 \rightarrow NO_2^- + O$  and the slope of the  $NO_2^-$  profile changes to 2. Around 1 sec, the rate of photodetachment exceeds the rate of the charge transfer, causing the  $NO_2^-$  to decay. The associative detachment reaction  $NO_2^- + O \rightarrow O_2 + NO + e$  also becomes effective in removing this ion around 50 secs, the time constant for this reaction. After 10 secs, the production falls off nearly as  $O^-$  decays while the photodetachment and associative detachment are removing this ion very rapidly, causing the sharp decrease between 10 and 100 secs. This removal continues until the rate of the charge transfer reaction again becomes equal to the rate of photodetachment and associative detachment and the  $NO_2^-$  concentration remains fixed at a constant ratio to the  $O^-$  concentration. The slight increase after  $10^4$  secs reflects the quasi-equilibrium dependence of this ion on the atomic oxygen concentration.

The atomic nitrogen starts to increase around  $10^{-4}$  secs because of the production of this atom by  $\text{NO}^+$  dissociative recombination. When the ionization starts to decay, this production stops, causing the atomic-nitrogen concentration to become constant again. The decay after  $10^4$  secs is caused by the increasing oxygen concentration in the recombination reaction  $\text{N} + \text{O} \rightarrow \text{NO} + h\nu$ . The behavior of the other minor neutral species is the same as given in the description of Figure 2.

## 5. THE DIURNAL VARIATION OF THE ATMOSPHERIC CONSTITUENTS

The basic code, as presented in Section 6.1, is ideally suited to such phenomena as the short-time effects on the atmosphere resulting from the detonation of nuclear weapons. The major source of the data on ionospheric parameters, however, is to be found in experimental studies of the natural ionosphere. These include ground-based probing techniques, measurements made in aircraft, and in situ measurements made with rockets. These experimental measurements cover most of the basic ionospheric characteristics of importance. In order to utilize these data for reaction-rate studies, for which this code is basically written, additions to the code are necessary so that it can solve the diurnal variation problem.

For this application it is required that the production of ionization by solar radiations be known as a function of the solar zenith angle. The code must also be capable of computing the local solar time for the location at which the computations are being made. The changes required in the deionization code for the computation of the diurnal variation of the atmospheric species are discussed in Section 7.2.

### 5.1 The Photoionization Source Function

In order to compute the diurnal variation of the atmospheric constituents, the production of ionization by direct and scattered solar radiation as well as that produced by cosmic rays is required.

Let  $\Phi_{\infty}(\Delta\lambda)$  be the photon flux incident on the top of the atmosphere and  $\Phi_z(\Delta\lambda)$  be the photon flux arriving at some height  $z$  in the wavelength region  $\Delta\lambda$ . Then

$$\Phi_z(\Delta\lambda) = \Phi_{\infty}(\Delta\lambda)e^{-\tau(\Delta\lambda)} \quad (16)$$

where  $\tau(\Delta\lambda)$  is the optical depth for energies in the wavelength region  $\Delta\lambda$ . If only atomic and molecular oxygen and molecular nitrogen are considered to be absorbers of this radiation, then the optical depth can be written as

$$\tau(\Delta\lambda) = \tau_O(\Delta\lambda) + \tau_{O_2}(\Delta\lambda) + \tau_{N_2}(\Delta\lambda) \quad (17)$$

The optical depth for each of the constituents is defined as

$$\tau_O(\Delta\lambda) = \sigma_O(\Delta\lambda) \cdot \int_z^\infty N(O) \cdot dl \quad (18)$$

$$\tau_{O_2}(\Delta\lambda) = \sigma_{O_2}(\Delta\lambda) \cdot \int_z^\infty N(O_2) \cdot dl \quad (19)$$

and

$$\tau_{N_2}(\Delta\lambda) = \sigma_{N_2}(\Delta\lambda) \cdot \int_z^\infty N(N_2) \cdot dl \quad (20)$$

where  $\sigma_O(\Delta\lambda)$ ,  $\sigma_{O_2}(\Delta\lambda)$ , and  $\sigma_{N_2}(\Delta\lambda)$  are the absorption cross sections for atomic oxygen, molecular oxygen, and molecular nitrogen respectively and the integrals represent the total number of the atoms or molecules in a  $\text{cm}^2$  column extending from  $z$  to infinity along the path  $l$ .

For computing the photoionization rates only those wavelengths capable of producing ionization have to be considered. The first ionization potential of  $O_2$  is at 1026.5Å, while the first ionization potential of  $O$  and  $N_2$  are at shorter wavelengths. In considering photoionization, therefore, it is necessary to take into account only energy fluxes at wavelength below 1026.5Å.

The primary electron production rate at altitude  $z$  resulting from the ionization of  $O$ ,  $O_2$ , and  $N_2$  in the wavelength region 1-1027Å can be written as

$$q = q(O^+) + q(O_2^+) + q(N_2^+) \quad (21)$$

$$q_{UV}(e) = \sum_{i=1}^3 q_i = \sum_{i=1}^3 \sum_{\Delta\lambda} N_i \sigma_i^1(\Delta\lambda) \Phi_\infty(\Delta\lambda) e^{-\left(\sum_{i=1}^3 \sigma_i(\Delta\lambda) \int_z^\infty N_i dl\right)} \quad (22)$$

where the  $\sigma_i^1(\Delta\lambda)$  are the ionization cross sections for the various constituents.

In addition to this, there are the electrons produced by the ionization of nitric oxide by  $L_\alpha$  at 1215.7A. The electron production rate resulting from this mechanism can be written as

$$q_{L_\alpha} = N(\text{NO}) \cdot \eta \sigma^i(\text{NO}) \cdot \Phi_{\infty}(L_\alpha) \cdot e - \left( \sigma(\text{O}_2) \cdot \int_z^\infty N(\text{O}_2) \cdot d1 \right) \quad (23)$$

since  $L_\alpha$  is absorbed by  $\text{O}_2$ . For  $L_\alpha$  the ionization cross section,  $\sigma^i(\text{NO})$ , according to Watanabe (1954), is  $2 \times 10^{-18} \text{cm}^2$  and the absorption cross section for molecular oxygen,  $\sigma(\text{O}_2)$ , according to Lee (1955) and Ditchburn, Bradley, Cannon, and Munday (1954), is  $8.5 \times 10^{-21} \text{cm}^2$ . A daytime flux of  $3 \text{ ergs/cm}^2/\text{sec}$  for  $L_\alpha$  is assumed for the numerical computations in this paper.

The production rate of electrons by energies in the 1-10A region is given by

$$q_X(e) = \sum_{i=1}^3 \sum_{\lambda} N_i K(\lambda) e - \left( \sum_{i=1}^3 \sigma_i(\lambda) \int_z^\infty N_i d1 \right) \quad (24)$$

where  $K(\lambda)$  is the ionization coefficient per molecule per sec at 2, 4, and 6A.

The production rate of electrons by cosmic rays used in this work is simply

$$q_{\text{CR}}(e) = 1.0 \times 10^{-16} \cdot N_z \quad (25)$$

where  $N_z$  is the total particle concentration at altitude .

The total daytime production rate of electrons is

$$q(e) = q_{\text{UV}}(e) + q_{L_\alpha}(e) + q_{\text{CR}}(e) + q_X(e) \quad (26)$$

During the night, in addition to the cosmic-ray flux, there is also some  $L_\alpha$  and  $L_\beta$  flux scattered in from the sunlit atmosphere. For the purpose of this work it was assumed that one percent of the noontime  $L_\alpha$  flux and 0.1 percent of the noontime  $L_\beta$  flux are available for the production of ionization during the night.

The photon fluxes in the 10-1027Å region are those reported by Hinteregger (1960). The 1-10Å X-ray ionization coefficients are taken from Nicolet and Aikin (1960) assuming slightly disturbed solar conditions. Table 1 shows the photon flux in each wavelength region and ionization and absorption cross sections for O, O<sub>2</sub>, and N<sub>2</sub>, as given by Hinteregger (1960). For broad spectral ranges, mean values of the ionization cross section are used. Because of the variation of the cross sections within a spectral range, especially for N<sub>2</sub>, several cross sections were used within the range with equal distribution of the total flux within the range over each of the subdivisions. The ionization efficiency factor is  $\eta$ . Its value is one for all wavelengths whose energies are less than 35 eV. For wavelengths with energies greater than 35 eV,  $\eta$  is given by  $\eta = \frac{E}{35}$  where E is the energy of the photon in eV.

Table 2 lists the concentrations of O, O<sub>2</sub>, and N<sub>2</sub> used to compute the column integrals. The concentrations above 80 km are taken from the COSPAR International Reference Atmosphere (1965). Concentrations below 80 km are taken from Keneshea (1963). A description of the photoionization code is given in Appendix A.

The electron production rate at noontime by the external production function is shown in Figure 5. Above 90 km, the ionization is by ultraviolet and soft X-rays. Around 90 km, the ionization is produced almost exclusively by X-rays in the 35Å region while around 80 km the production is primarily the result of the ionization of NO by L<sub>α</sub>. By 60 km, the production results solely from cosmic-ray ionization.

Figure 6 shows the electron-ion production rates at noontime by the external source function. Above 90 km, the O<sub>2</sub><sup>+</sup> ion is the most abundant ion produced. At 70 and 80 km, the production of NO<sup>+</sup> ions by L<sub>α</sub> predominates.

## 5.2 The Simplified Sunrise-Sunset Function

Because of the rapid changes in the concentrations of some of the atmospheric constituents during sunrise and sunset, more realistic results are obtained with the code if the sun is considered to be an extended source rather than a point source. It is necessary, therefore, to consider the geometry of a moving disc obscured by a plane. Because the viewing angle of the earth is much larger than the viewing angle of the sun to an observer in the ionosphere, the earth's horizon is considered to be flat.

In order to handle this problem correctly, it is necessary to take into account the absorption of the specific wavelengths responsible for the photodetachment of each negative ion and the photodissociation of each neutral species. Unfortunately, the spectral dependence of these processes for all the negative ions and neutral constituents is not known. For the purposes of this paper, therefore, the full daylight coefficients for photodetachment and photo-dissociation are simply modified by the percentage of the total visible light transmitted as the sun rises or sets.

Table 1. Solar Flux Data, Ionization Cross Sections, and Absorption Cross Sections  
 (Data of H. E. Hinteregger GRD Technical Note 39, AFRL-TN-60-485, 1960)

Wavelength A	Photon Flux, 10 <sup>8</sup> /cm <sup>2</sup> /sec	$\eta \sigma'(O_2)$ 10 <sup>-18</sup> cm <sup>2</sup>	$\sigma(O_2)$ 10 <sup>-18</sup> cm <sup>2</sup>	$\eta \sigma'(O)$ 10 <sup>-18</sup> cm <sup>2</sup>	$\sigma(O)$ 10 <sup>-18</sup> cm <sup>2</sup>	$\eta \sigma'(N_2)$ 10 <sup>-18</sup> cm <sup>2</sup>	$\sigma(N_2)$ 10 <sup>-18</sup> cm <sup>2</sup>
1025.7	26	1	1.7	0	0	0	0
1000-1027	15	1	1.5	0	0	0	0
989.8	5	1.8	2.2	0	0	0	0
977.0	30	3	3.7	0	0	0	0.8
972.5	10	25	30	0	0	0	280
949.7	5	5	5.6	0	0	0	1.9
911-1000	7.4	6	7.4	0	0	0	40
	7.4	6	7.4	0	0	0	10
	7.4	6	7.4	0	0	0	5
	7.4	6	7.4	0	0	0	1
	7.4	6	7.4	0	0	0	0.4
850-911	19	9	11	3	3	0	40
	19	9	11	3	3	0	10
	19	9	11	3	3	0	5
	19	9	11	3	3	0	1
	19	9	11	3	3	0	0.4
796-850	5	9	11	3.5	3.5	0	40
	5	9	11	3.5	3.5	0	10
	5	9	11	3.5	3.5	0	5
	5	9	11	3.5	3.5	0	1
	5	9	11	3.5	3.5	0	0.4
700-796	16.6	15	18	5	5	9	11
	16.6	15	18	5	5	15	19
	16.6	15	18	5	5	30	37
600-700	15.6	15	18	10	10	9	11
	15.6	15	18	10	10	15	19
	15.6	15	18	10	10	30	37
584.3	29	15	18	13	13	15	19

Table 1 (Continued)

Wavelength A	Photon Flux, $10^8/\text{cm}^2/\text{sec}$	$\eta \sigma^1(\text{O}_2)$ $10^{-18}\text{cm}^2$	$\sigma(\text{O}_2)$ $10^{-18}\text{cm}^2$	$\eta \sigma^1(0)$ $10^{-18}\text{cm}^2$	$\sigma(0)$ $10^{-18}\text{cm}^2$	$\eta \sigma^1(\text{N}_2)$ $10^{-18}\text{cm}^2$	$\sigma(\text{N}_2)$ $10^{-18}\text{cm}^2$
500-600	10	15	18	15	15	9	11
	10	15	18	15	15	15	19
	10	15	18	15	15	30	37
400-500	8	15	18	11	11	9	11
	8	15	18	11	11	15	19
	8	15	18	11	11	30	37
303.8	43	19.9	17	11.7	10	11.7	10
300-400	15	16.2	16	10.1	10	11.1	11
	15	16.2	16	10.1	10	19.2	19
230-300	31	20.1	15	12.1	9	12.1	9
170-230	33	19.5	11	12.4	7	10.6	6
110-170	3.5	5.33	2.1	2.54	1	12.7	5
80-110	4.5	6.62	1.77	3.33	0.89	3.74	1
60-80	2.8	4.92	0.97	2.48	0.49	2.86	0.565
45-60	1.8	2.7	0.4	1.35	0.2	1.55	0.23
35-45	1.1	0.887	0.19	0.842	0.095	0.976	0.11
30-35	0.5	0.983	0.09	0.491	0.045	0.568	0.052
20-30	0.12	6.39	0.45	3.27	0.23	13.3	0.94
10-20	0.02	11	0.467	5.51	0.233	7.97	0.337



Table 2. Concentrations of Neutral Species

Altitude (km)	N(O)/CC	N(O <sub>2</sub> )/CC	N(N <sub>2</sub> )/CC
0	0	5.34×10 <sup>18</sup>	1.99×10 <sup>19</sup>
10	1.00×10 <sup>5</sup>	1.80×10 <sup>18</sup>	6.71×10 <sup>18</sup>
20	1.50×10 <sup>8</sup>	3.00×10 <sup>17</sup>	1.40×10 <sup>18</sup>
30	1.20×10 <sup>10</sup>	7.00×10 <sup>16</sup>	3.15×10 <sup>17</sup>
40	2.40×10 <sup>10</sup>	1.70×10 <sup>16</sup>	7.60×10 <sup>16</sup>
50	3.50×10 <sup>10</sup>	5.00×10 <sup>15</sup>	1.80×10 <sup>16</sup>
60	4.80×10 <sup>10</sup>	1.50×10 <sup>15</sup>	5.70×10 <sup>15</sup>
70	6.40×10 <sup>10</sup>	7.53×10 <sup>14</sup>	1.60×10 <sup>15</sup>
80	8.50×10 <sup>10</sup>	7.95×10 <sup>13</sup>	2.96×10 <sup>14</sup>
90	1.25×10 <sup>11</sup>	1.33×10 <sup>13</sup>	4.97×10 <sup>13</sup>
100	5.00×10 <sup>11</sup>	1.99×10 <sup>12</sup>	8.18×10 <sup>12</sup>
110	2.00×10 <sup>11</sup>	3.49×10 <sup>11</sup>	1.62×10 <sup>12</sup>
120	7.60×10 <sup>10</sup>	7.46×10 <sup>10</sup>	4.01×10 <sup>11</sup>
130	3.67×10 <sup>10</sup>	2.34×10 <sup>10</sup>	1.40×10 <sup>11</sup>
140	2.16×10 <sup>10</sup>	9.79×10 <sup>9</sup>	6.36×10 <sup>10</sup>
150	1.42×10 <sup>10</sup>	4.78×10 <sup>9</sup>	3.34×10 <sup>10</sup>
160	9.84×10 <sup>9</sup>	2.56×10 <sup>9</sup>	1.91×10 <sup>10</sup>
170	7.15×10 <sup>9</sup>	1.47×10 <sup>9</sup>	1.16×10 <sup>10</sup>
180	5.36×10 <sup>9</sup>	8.83×10 <sup>8</sup>	7.37×10 <sup>9</sup>
190	4.12×10 <sup>9</sup>	5.52×10 <sup>8</sup>	4.85×10 <sup>9</sup>
200	3.23×10 <sup>9</sup>	3.57×10 <sup>8</sup>	3.29×10 <sup>9</sup>
210	2.58×10 <sup>9</sup>	2.37×10 <sup>8</sup>	2.29×10 <sup>9</sup>
220	2.09×10 <sup>9</sup>	1.61×10 <sup>8</sup>	1.62×10 <sup>9</sup>
230	1.71×10 <sup>9</sup>	1.11×10 <sup>8</sup>	1.17×10 <sup>9</sup>
240	1.41×10 <sup>9</sup>	7.75×10 <sup>7</sup>	8.51×10 <sup>8</sup>
250	1.18×10 <sup>9</sup>	5.49×10 <sup>7</sup>	6.28×10 <sup>8</sup>
260	9.89×10 <sup>8</sup>	3.92×10 <sup>7</sup>	4.67×10 <sup>8</sup>
270	8.33×10 <sup>8</sup>	2.82×10 <sup>7</sup>	3.50×10 <sup>8</sup>
280	7.06×10 <sup>8</sup>	2.05×10 <sup>7</sup>	2.64×10 <sup>8</sup>
290	6.00×10 <sup>8</sup>	1.50×10 <sup>7</sup>	2.00×10 <sup>8</sup>
300	5.12×10 <sup>8</sup>	1.10×10 <sup>7</sup>	1.52×10 <sup>8</sup>
310	4.38×10 <sup>8</sup>	8.23×10 <sup>6</sup>	1.17×10 <sup>8</sup>
320	3.70×10 <sup>8</sup>	5.80×10 <sup>6</sup>	8.67×10 <sup>7</sup>
330	3.22×10 <sup>8</sup>	4.50×10 <sup>6</sup>	6.90×10 <sup>7</sup>
340	2.74×10 <sup>8</sup>	3.20×10 <sup>6</sup>	5.14×10 <sup>7</sup>

Table 2 (Continued)

Altitude (km)	N(O)/CC	N(O <sub>2</sub> )/CC	N(N <sub>2</sub> )/CC
350	2.39×10 <sup>8</sup>	2.49×10 <sup>6</sup>	4.11×10 <sup>7</sup>
360	2.04×10 <sup>8</sup>	1.78×10 <sup>6</sup>	3.08×10 <sup>7</sup>
370	1.78×10 <sup>8</sup>	1.39×10 <sup>6</sup>	2.46×10 <sup>7</sup>
380	1.52×10 <sup>8</sup>	1.00×10 <sup>6</sup>	1.85×10 <sup>7</sup>
390	1.33×10 <sup>8</sup>	7.82×10 <sup>5</sup>	1.49×10 <sup>7</sup>
400	1.14×10 <sup>8</sup>	5.65×10 <sup>5</sup>	1.13×10 <sup>7</sup>
410	1.00×10 <sup>8</sup>	4.43×10 <sup>5</sup>	9.04×10 <sup>6</sup>
420	8.59×10 <sup>7</sup>	3.20×10 <sup>5</sup>	6.83×10 <sup>6</sup>
430	7.53×10 <sup>7</sup>	2.52×10 <sup>5</sup>	5.51×10 <sup>6</sup>
440	6.49×10 <sup>7</sup>	1.83×10 <sup>5</sup>	4.19×10 <sup>6</sup>
450	5.70×10 <sup>7</sup>	1.44×10 <sup>5</sup>	3.38×10 <sup>6</sup>
460	4.91×10 <sup>7</sup>	1.05×10 <sup>5</sup>	2.58×10 <sup>6</sup>
470	4.32×10 <sup>7</sup>	8.30×10 <sup>4</sup>	2.09×10 <sup>6</sup>
480	3.73×10 <sup>7</sup>	6.06×10 <sup>4</sup>	1.59×10 <sup>6</sup>
490	3.28×10 <sup>7</sup>	4.74×10 <sup>4</sup>	1.29×10 <sup>6</sup>
500	2.83×10 <sup>7</sup>	3.51×10 <sup>4</sup>	9.86×10 <sup>5</sup>
510	2.50×10 <sup>7</sup>	2.72×10 <sup>4</sup>	8.00×10 <sup>5</sup>

The area of a sector of the circle in Figure 7 subtended by the angle  $\theta$  is  $\frac{r^2\theta}{2}$ . From Figure 7

$$\cos\left(\frac{\theta}{2}\right) = \frac{r-x}{r} \quad (27)$$

Since

$$\cos 2u = 2 \cos^2 u - 1 \quad (28)$$

then

$$\cos \theta = 2 \left(\frac{r-x}{r}\right)^2 - 1 \quad (29)$$

or

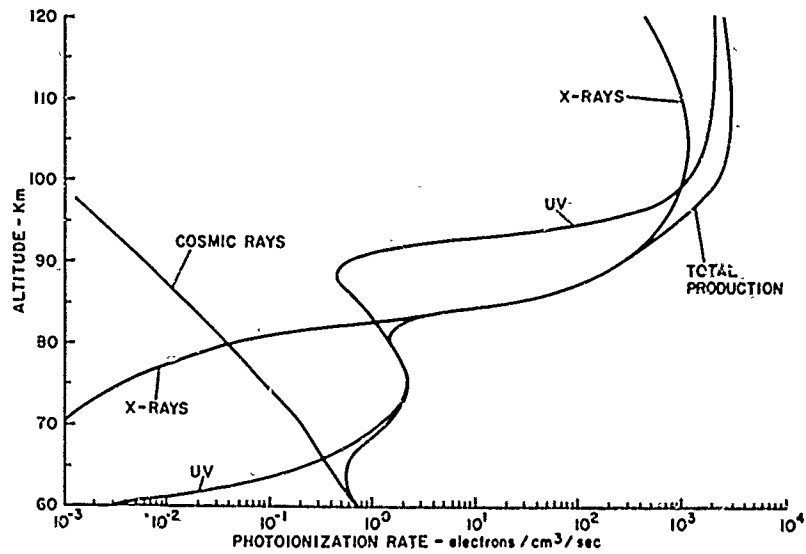


Figure 5. Electron Production Rates by Extraterrestrial Radiations (Brazil noontime)

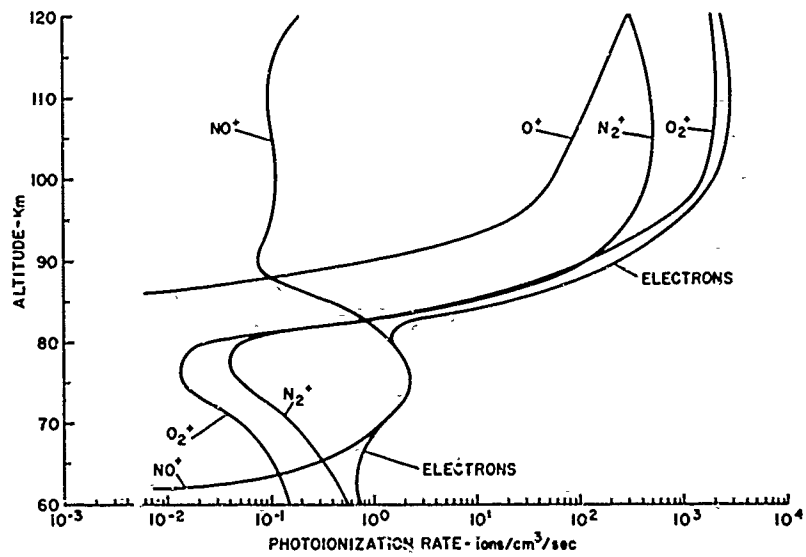


Figure 6. Electron-Ion Production Rates by Extraterrestrial Radiation (Brazil noontime)

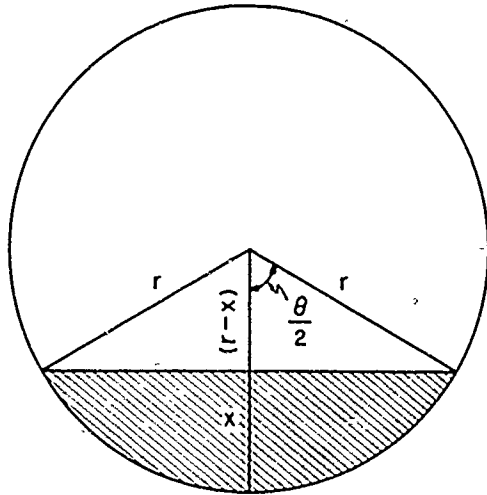


Figure 7. Sunrise-Sunset Geometry

$$\theta = \cos^{-1} \left[ 2 \left( \frac{r-x}{r} \right)^2 - 1 \right] \quad (30)$$

The area of the two triangles in Figure 7 is

$$(r-x) r \sin\left(\frac{\theta}{2}\right) \quad (31)$$

which can be written as

$$(r-x) r \left[ \frac{1-\cos \theta}{2} \right]^{1/2} \quad (32)$$

The shaded area of the sector is

$$A = \frac{r^2 \theta}{2} - (r-x) r \left[ \frac{1-\cos \theta}{2} \right]^{1/2} \quad (33)$$

Let r equal one solar radius, then

$$A = \frac{\theta}{2} - (1-x) \left[ \frac{1-\cos \theta}{2} \right]^{1/2} \quad (34)$$

where

$$\cos \theta = 2(1-x)^2 - 1 \quad (35)$$

The transmissivity factor,  $\eta$ , can be written as

$$\eta = 1 - \frac{\Lambda}{\pi r^2} \quad (36)$$

which for  $r=1$  becomes

$$\eta = 1 - \frac{\Lambda}{\pi} \quad (37)$$

or

$$\eta = 1 - \left\{ \frac{\left[ \frac{\theta}{2} - (1-x) \left| \frac{1-\cos \theta}{2} \right|^{1/2} \right]}{\pi} \right\} \quad (38)$$

### 5.3 Diurnal Variation Results

In computing the diurnal variation some changes in the basic list of reaction rates are necessary in order to obtain solutions that are generally consistent with available experimental evidence. An attempt was made to achieve the  $\text{NO}^+/\text{O}_2^+$  daytime ratios observed by Narcisi (1966). There is, of course, no unique way to obtain these ratios in the present system. In the E region they can be achieved by varying the rate constant for the charged rearrangement reaction  $\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$ . They can also be arrived at by using a different concentration of atomic nitrogen for this reaction. This ratio is also sensitive to the ratio of the rate constants for  $\text{NO}^+$  and  $\text{O}_2^+$  dissociative recombination. Because of the recent measurements by Furguson et al. (1965) of the rate constant for the charged rearrangement reaction and because of the lack of experimental measurements of the concentration of atomic nitrogen, the first two choices were rejected. In order to establish ratios consistent with those of Narcisi (1966), the rate constant for  $\text{NO}^+$  dissociative recombination is made equal to that for  $\text{O}_2^+$  dissociative recombination.

In addition to the other rate constant adjustments discussed in Section 4, the rate constants for four more reactions are changed for the diurnal variation runs. The associative detachment reaction  $\text{O}_3^- + \text{O} \rightarrow 2\text{O}_2 + e$  is an important reaction in the electron kinetics in the D region. Allowing this detachment to take place produces profiles at night that are contrary to experimental observations. An example of this behavior is presented in Section 6. The rate constant for this reaction and the similar reaction for  $\text{NO}_2^- + \text{O} \rightarrow \text{O}_2 + \text{NO} + e$  were therefore set to zero. Problems then arose in trying to obtain a negative ion-to-electron ratio of unity at 70 km. To accomplish this the rate coefficient for  $\text{O}_3^-$  photo-detachment is changed to 1.4 and the rate constant for the charge transfer reaction  $\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2$  is changed to  $7.77 \times 10^{-9}$ . With these rate constant changes, reasonable negative ion-to-electron ratios are obtained at noontime in the D region.

Because the energy available in the Herzberg continuum was not considered in this work and because all of the energy in the Schumann continuum is absorbed above 100 km, no photodissociation of  $O_2$  is allowed below 110 km. The incorporation of  $O_2$  photodissociation into the code is discussed in Section 7.2.1.1. When viewing the atomic oxygen profiles, this fact should be kept in mind.

Before discussing the actual diurnal variations of the various atmospheric species in the D and E ionospheric regions, it might be worthwhile to study the kinetics of the reactions responsible for the noontime profiles of the more important ionic and neutral constituents.

### 7.3.1 THE NOONTIME KINETICS

The diurnal variations were computed in height intervals of 10 km and at noontime a snapshot was taken of the rates at which the individual reactions were proceeding. From this output the reactions contributing predominantly to the kinetics of each species were extracted. The height profiles of the rates at which these reactions were proceeding are shown in Figures 8 through 16 for the major species.

The electron kinetics are shown in Figure 8. Above 90 km, the electron concentration results from the equilibrium established between the electrons produced by the external source and those lost by dissociative recombination with  $O_2^+$  and  $NO^+$ . Below 80 km, the picture is entirely different. Here the electron concentration is determined by the equilibrium established between the production of electrons by photodetachment from negative ions and the three-body attachment of the electrons to  $O_2$ . The altitudes between 80 and 90 km are transition altitudes where the electron concentration results equally from the external source and the photodetachment productions and the dissociative recombination and three-body attachment removals.

Figure 9 shows the kinetics of  $O^-$ . Above 90 km, this ion is produced solely by the radiative attachment of electrons to atomic oxygen. Above 110 km the only removal process for these ions is the photodetachment, while below 100 km the associative detachment  $O^- + N_2 \rightarrow N_2O + e$  becomes the only removal mechanism. There is some controversy as to whether this reaction is endothermic or exothermic. Bortner (1965) discussed this problem and accepted the thermochemical data that makes this process exothermic. Below 90 km the  $O^-$  ions are produced by the charge transfer between  $O_2^-$  and atomic oxygen and by the dissociative attachment reaction  $O_3 + e \rightarrow O^- + O_2$ .

From Figure 10 it is obvious that the formation of  $O_2^-$  ions over the entire altitude range is by the three-body attachment of electrons to  $O_2$ . Above 80 km they are removed by photodetachment and by the charge transfer between  $O_2^-$  and atomic oxygen. Below 80 km the predominant removal process becomes the charge transfer between  $O_2^-$  and ozone.

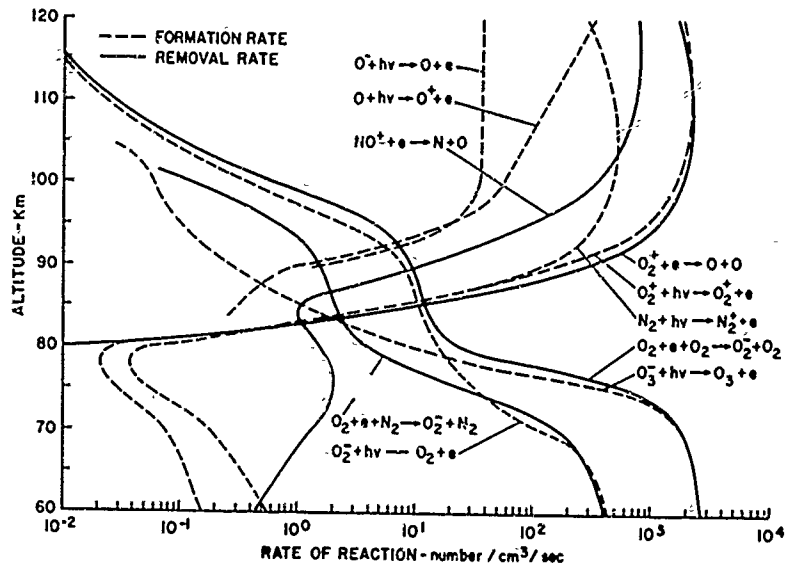


Figure 8. Important Processes for Electrons (Brazil noontime)

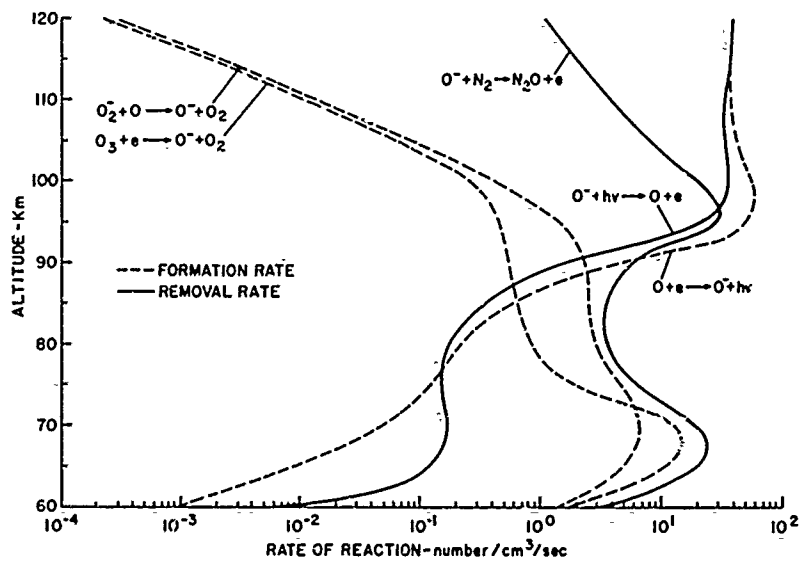


Figure 9. Important Processes for  $O^-$  (Brazil noontime)

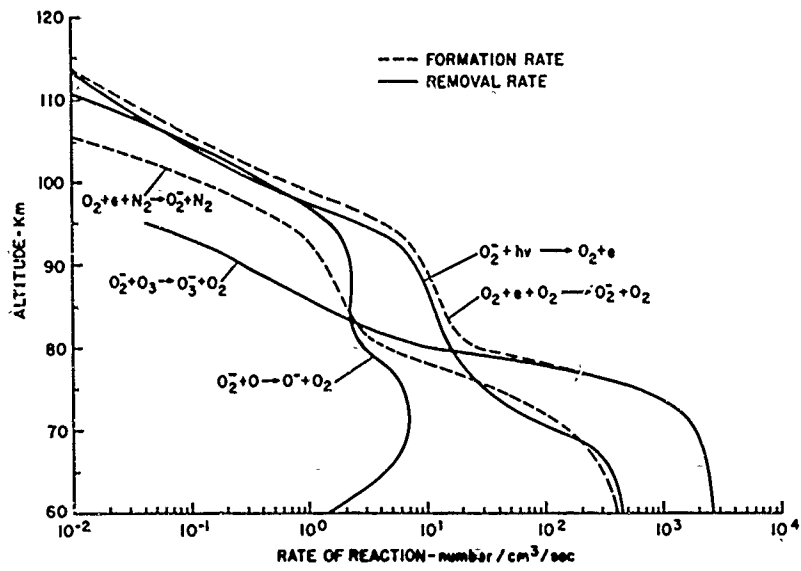


Figure 10. Important Processes for  $O_2^-$  (Brazil noontime)

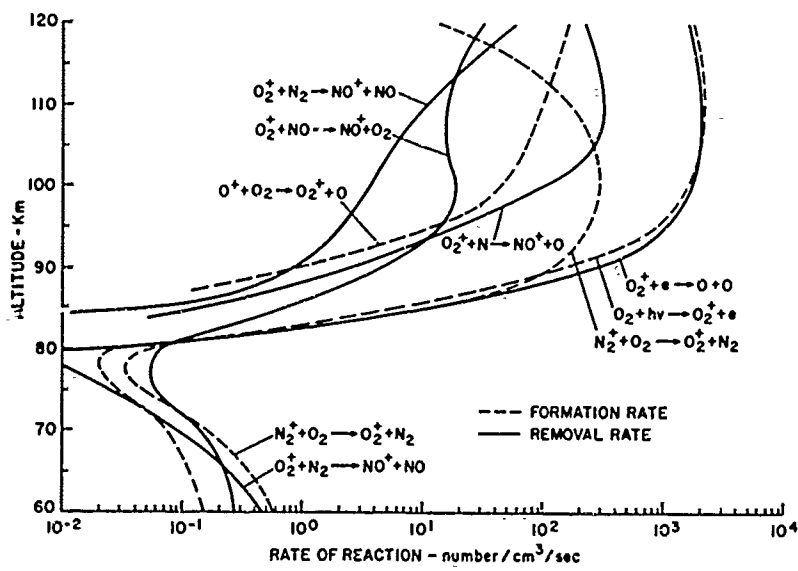


Figure 11. Important Processes for  $O_2^+$  (Brazil noontime)



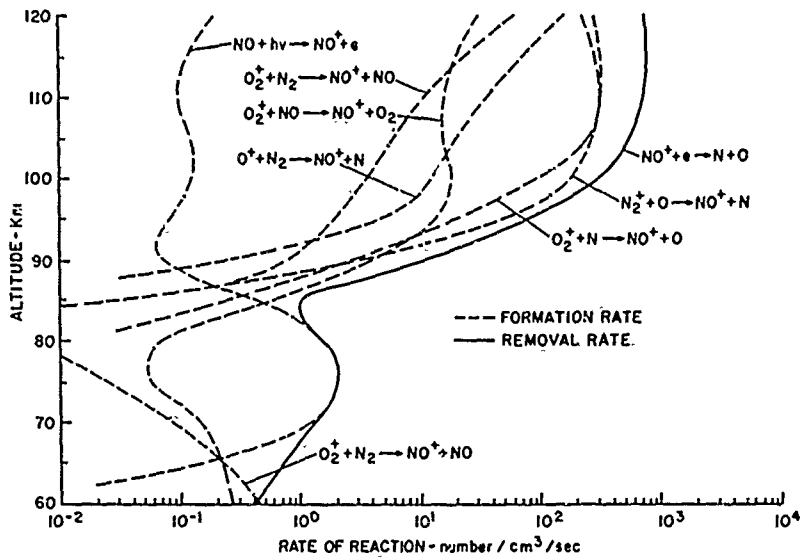


Figure 12. Important Processes for  $\text{NO}^+$  (Brazil noontime)

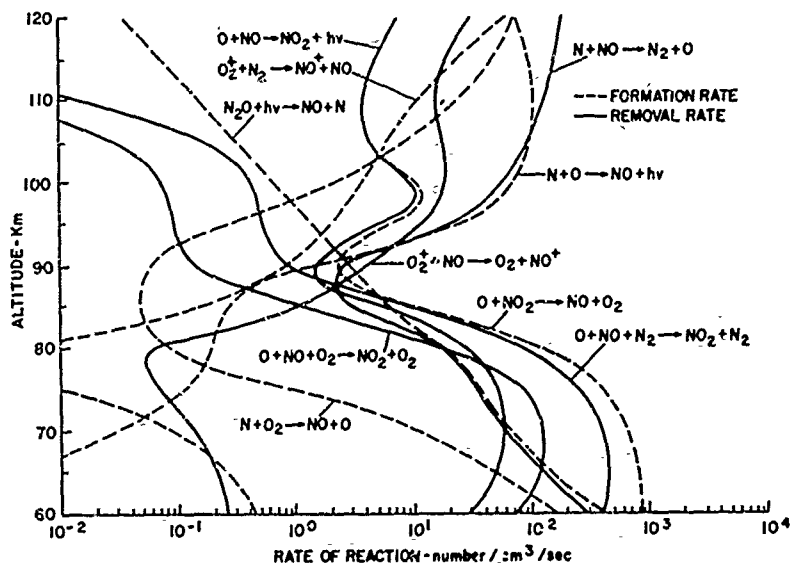


Figure 13. Important Processes for Nitric Oxide (Brazil noontime)

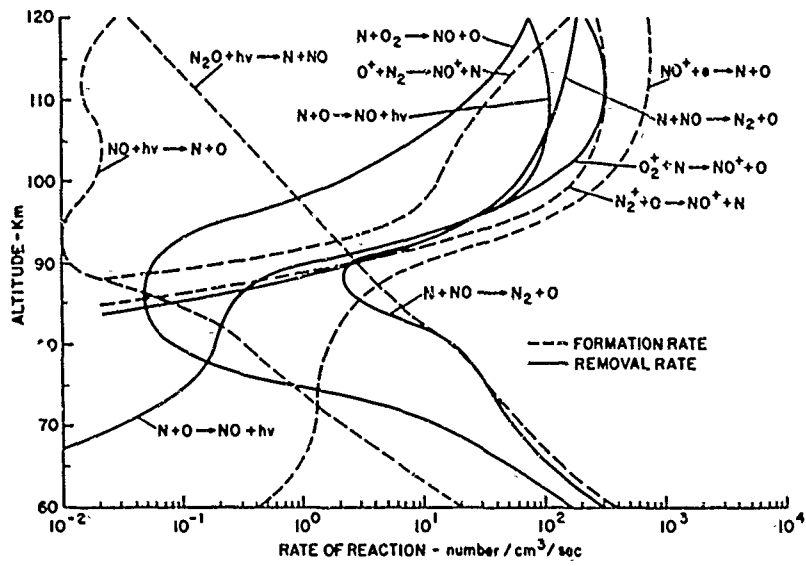


Figure 14. Important Processes for Atomic Nitrogen (Brazil noontime)

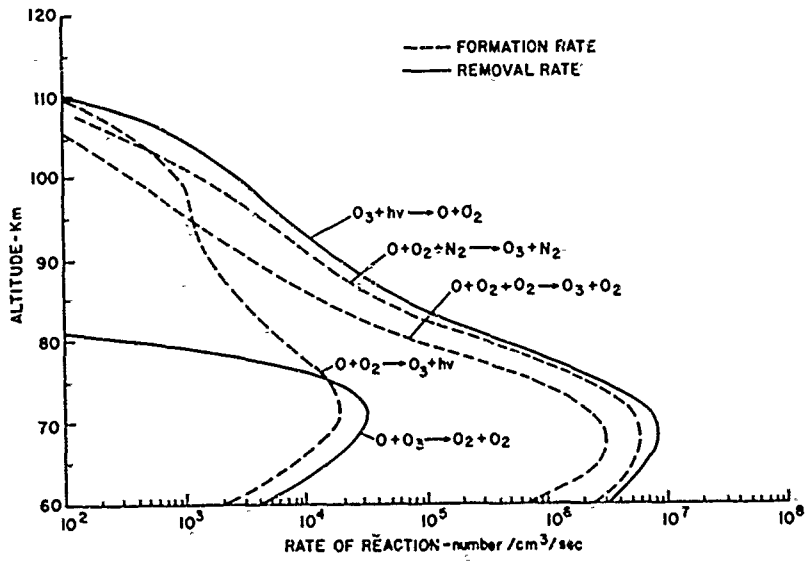


Figure 15. Important Processes for Ozone (Brazil noontime)

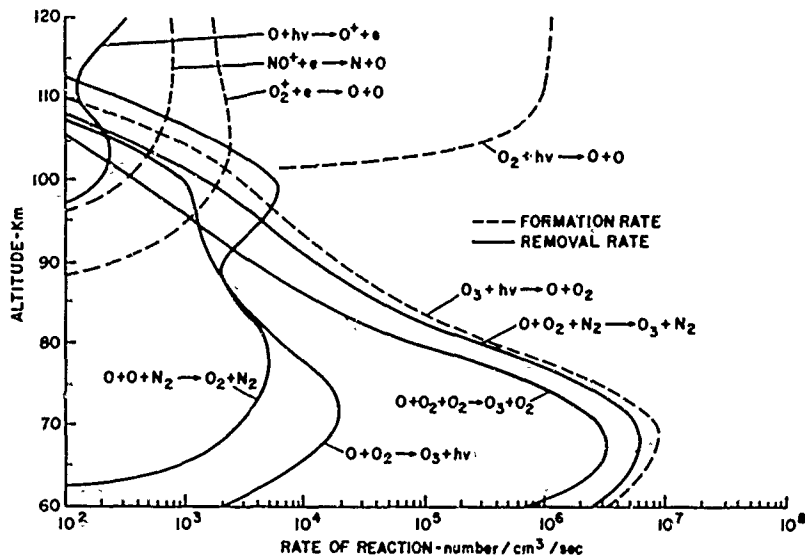


Figure 16. Important Processes for Atomic Oxygen (Brazil noontime)

The kinetics of the  $O_2^+$  ions are shown in Figure 11. Above 80 km these ions are removed almost entirely by dissociative recombination. In the E region they are formed primarily by photoionization. Below 90 km the charge transfer process  $N_2^+ + O_2 \rightarrow O_2^+ + N_2$  and the external source contribute about equally to the production of this ion. Below 80 km  $O_2^+$  becomes a minor ion since it is produced by cosmic-ray ionization and from  $N_2^+$  by charge transfer while the latter ions are being formed in small numbers by cosmic-ray ionization. The  $O_2^+$  ions react to form  $NO^+$  ions below 80 km by charged rearrangement with  $N_2$  and charge transfer with  $NO$ .

Figure 12 shows the processes responsible for the noontime kinetics of  $NO^+$ . The only removal process that is important at all altitudes is the dissociative recombination. Above 85 km  $NO^+$  is formed primarily from  $O_2^+$  and  $N_2^+$  by charged rearrangement with atomic oxygen and atomic nitrogen respectively. Of lesser importance are the  $O_2^+$  charged rearrangement with  $N_2$ , the charge transfer between  $O_2^+$  and  $NO$  and the charged rearrangement between  $O^+$  and  $N_2$ . Between 70 and 80 km this ion is formed almost exclusively by the ionization of  $NO$  by  $L_\alpha$ .

The kinetics of nitric oxide are shown in Figure 13. The neutral rearrangement reaction  $N + NO \rightarrow N_2 + O$  is an important removal process for this molecule at all altitudes. The two-body atom recombination  $N + O \rightarrow NO + h\nu$  is important in forming this molecule above 90 km. Below this altitude it becomes unimportant

because of the relatively small amounts of atomic nitrogen available. The abundance of  $O_2^+$  ions in the E region makes the charge transfer to NO also important above 90 km. Below 80 km these molecules are formed by the neutral rearrangement process  $O + NO_2 \rightarrow NO + O_2$  and by the photodissociation of  $N_2O$ . They are removed by the three-body atom recombination  $O + NO + M \rightarrow NO_2 + M$  and by the atom recombination  $O + NO \rightarrow NO_2 + h\nu$ . The minimum in the rate of the process  $N + O_2 \rightarrow NO + O$  between 80 and 90 km is produced by the temperature dependence of the rate constant for this process which is a minimum in this region.

The kinetics of atomic nitrogen, as shown in Figure 14, are influenced mainly by charged species reactions above 90 km and by neutral reactions below this altitude. In the E layer it is produced primarily by the dissociative recombination of  $NO^+$  and by the charged rearrangement between  $N_2^+$  and atomic oxygen. Its major removal process is the charged rearrangement with  $O_2^+$ . Also contributing to its removal are its neutral rearrangement with NO and its recombination with atomic oxygen. In the D region this atom is formed by the photodissociation of  $N_2O$  and of NO. It is removed by the neutral rearrangement reactions  $N + NO \rightarrow N_2 + O$  and  $N + O_2 \rightarrow NO + O$ .

Figure 15 shows the kinetics for ozone at noontime. The primary removal mechanism for this molecule is photodissociation. Also contributing to its removal is the neutral rearrangement reaction  $O + O_3 \rightarrow 2O_2$ . The major formation of ozone is by the three-body recombination  $O + O_2 + M \rightarrow O_3 + M$ . Of minor importance in forming ozone is the two-body atom recombination  $O + O_2 \rightarrow O_3 + h\nu$ . The rates for the three-body recombination processes fall off rapidly with increasing altitude because of the decreasing molecular concentrations.

The important reactions for atomic oxygen are shown in Figure 16. In the D region the atomic oxygen kinetics are controlled by the same reactions as the ozone concentration. In the E region the photodissociation of molecular oxygen is the major source of oxygen atoms. There is no effective chemical removal of these atoms during the daytime in the E region.

### 5.3.2 THE DIURNAL VARIATIONS

The code, as discussed in Section 6.2, was used to compute the time histories of the 15 atmospheric species incorporated into the code. Many concentration profiles were computed for various geographic locations. From these computations those made for the coordinates 32.197° S and 52.169° W were chosen for presentation here. This location is in Brazil where sounding rockets were launched during the eclipse of 12 November 1966.

The diurnal variation profiles are generated in the following manner. The code is started at local noon with the concentrations of the charged species initially set to zero and the concentrations of the neutral species initially set to best estimate values.

The code is then run through one diurnal cycle (24 hours). Taking the concentrations of all the species at the end of this diurnal cycle as initial conditions, a solution is generated over a second diurnal cycle. The profiles computed over this second diurnal cycle are presented here.

Technically, this procedure should be repeated over as many diurnal cycles as are required to achieve equilibrium profiles. Equilibrium, as defined here, is achieved when the variation in the concentration of each species reproduces itself over succeeding diurnal cycles. In the profiles presented, it is apparent that for some of the species this equilibrium was not achieved in the second cycle and more diurnal cycles should have been computed. Nevertheless, this does not diminish the validity of the results as they are discussed.

Figure 17 shows the diurnal variation of the major charged species at 120 km. Although the variation of all nine charged species in the code were computed, only those species that attain concentrations above  $10 \text{ particles/cm}^3$  are plotted. The noontime value of the electron concentration results from the equilibrium established between the production by photoionization and the dissociative recombination of  $\text{O}_2^+$  and  $\text{NO}^+$ . As the solar zenith angle increases, the rate of production decreases because of the greater attenuation of the solar radiations through the denser columns in the atmosphere. The production rate is reduced to its nighttime value about a half hour before the sun starts to set. As fewer electrons are produced, those already made are removed by recombination, causing the concentrations of the electrons and the positive ions to decrease. This decay continues until the production rate is reduced to its constant nighttime value at which time a new equilibrium is established for the electrons and the  $\text{NO}^+$  ions. The  $\text{O}_2^+$  concentration decays below the  $\text{NO}^+$  concentration because of the conversion of  $\text{O}_2^+$  ions into  $\text{NO}^+$  ions by the charged rearrangement reaction  $\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$ . The  $\text{O}_2^+$  concentration increases during the night because the rate of removal by the charged rearrangement reaction  $\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$  decreases with the decreasing atomic nitrogen concentration. After the sun rises and the ionizing radiation starts to penetrate to this altitude, the production of ionization increases, causing the concentration to increase until the production rate levels off around noontime and the daytime equilibrium is established between the production of ionization and the dissociative recombination.

Figure 18 shows the diurnal profiles for the neutral species at 120 km. Atomic oxygen was not plotted here because its concentration varies only slightly around  $2 \times 10^{11} \text{ atoms/cm}^3$ . During the daytime the concentration of atomic nitrogen builds up as it is formed by the dissociative recombination  $\text{NO}^+ + e \rightarrow \text{N} + \text{O}$  and by the charged rearrangement  $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$  at a faster rate than it is removed by the charged rearrangement  $\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$  or the neutral rearrangement  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . During the night, however, the formation by the

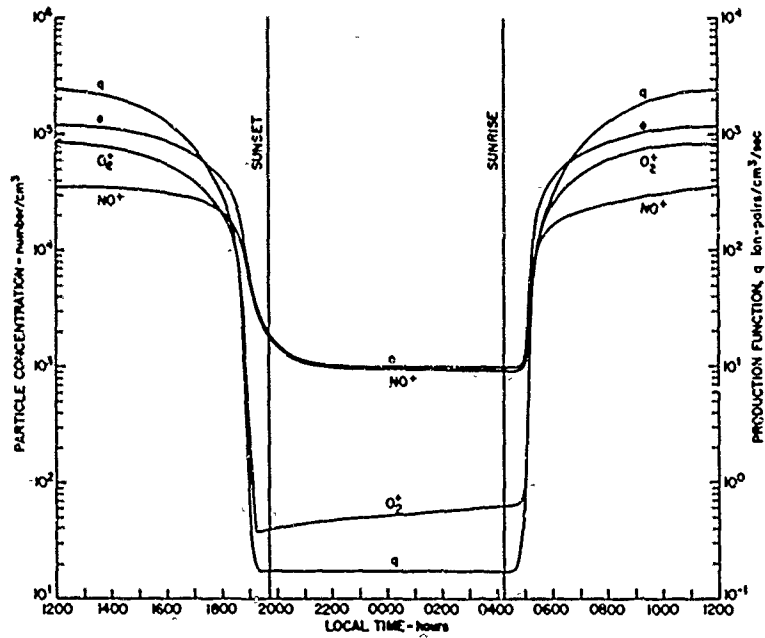


Figure 17. Diurnal Variation of Charged Species at 120 km (Brazil noontime)

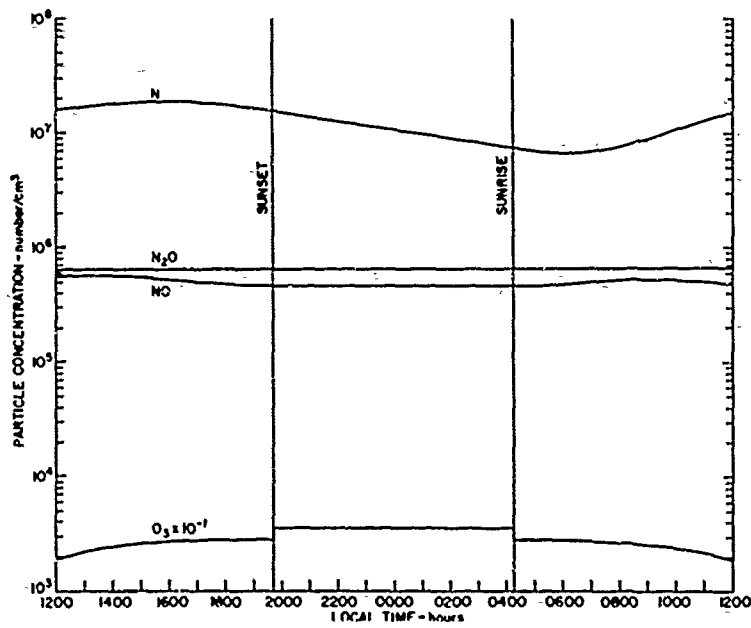


Figure 18. Diurnal Variation of Neutral Species at 120 km (Brazil noontime)

dissociative recombination and the charged rearrangement practically stops. The only process really affecting this atom then is the neutral rearrangement which causes its concentration to decay steadily throughout the night. No change is possible in the  $N_2O$  concentration because the time constant for its removal by photodissociation is about  $10^5$  secs which is longer than one day. There is no effective formation or removal process for this molecule at night. The slight diurnal variation in nitric oxide is caused by the diurnal variation of  $O_2^+$  in the process  $O_2^+ + N_2 \rightarrow NO^+ + NO$ . Ozone is only a trace species at 120 km. The slight variation in its concentration is caused by the variation of its rate of photodissociation with the solar zenith angle. When the photodissociation stops at sunset its concentration increases by the two-body recombination reaction  $O + O_2 \rightarrow O_3 + h\nu$  until a new equilibrium is established between this recombination and the neutral rearrangement reaction  $O + O_3 \rightarrow O_2 + O_2$ .

Figure 19 shows the diurnal variation of the major charged species at 110 km. The behavior of the charged species at this altitude is similar to that at 120 km. The noontime equilibrium value of the electrons is slightly lower here than at 120 km because of the slightly larger recombination rate constants. Since these rate constants are inversely proportional to the temperature, their values are higher at 110 km than at 120 km because of the decreased temperature. The nighttime concentrations are a little higher than they are at 120 km because the nighttime production function is larger at this altitude.

The only real difference in the neutral species profiles at 110 km, as shown in Figure 20, from those at 120 km is the ozone profile. Since the rate of the three-body recombination process  $O + O_2 + M \rightarrow O_3 + M$  is increasing with decreasing altitude, more ozone molecules are formed at this altitude at night when their photodissociation has stopped.

The charged species diurnal variations at 100 km, as shown in Figure 21, display much of the same behavior that is seen at the two higher altitudes. The slightly lower concentrations reflect the slightly lower photoionization rate. At night, however, at this altitude  $O_3^-$  starts to become an important negative ion. Because of the increase in the concentration of ozone during the night, the rate of the dissociative attachment reaction  $O_3 + e \rightarrow O^- + O_2$  increases. However, the charge transfer reaction  $O^- + O_3 \rightarrow O_3^- + O$  proceeds so rapidly because of the increased  $O_3$  concentration that the  $O^-$  ions created by attachment immediately transfer their charge to  $O_3$ , causing the electrons to decay slightly as their charge goes into the formation of  $O_3^-$  ions. As soon as the sun starts to rise, however, the electrons are very quickly detached from the  $O_3^-$  ions, causing the concentration of this ion to decay rapidly with a corresponding increase in the electron concentration.

Figure 22 shows the diurnal variation of the minor neutral species at 100 km. Their behavior is again similar to that at the higher altitudes. There is, however,

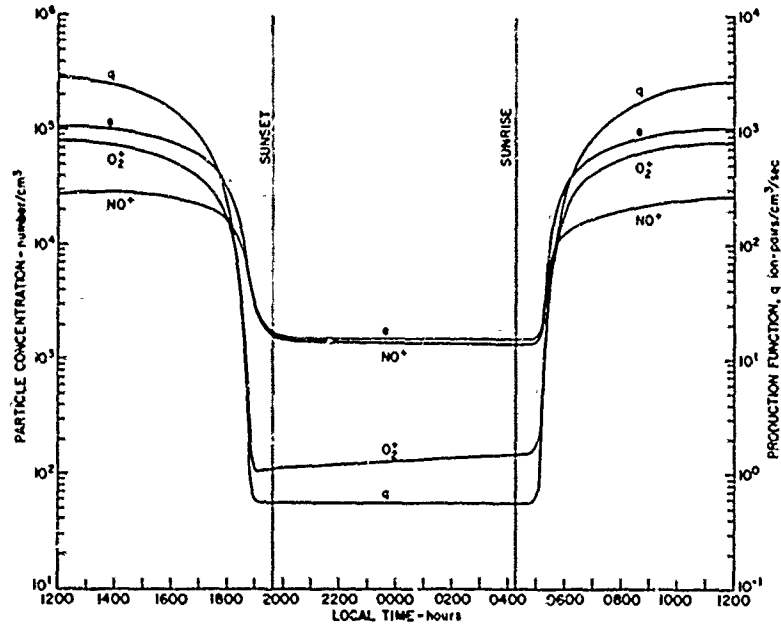


Figure 19. Diurnal Variation of Charged Species at 110 km (Brazil noontime)

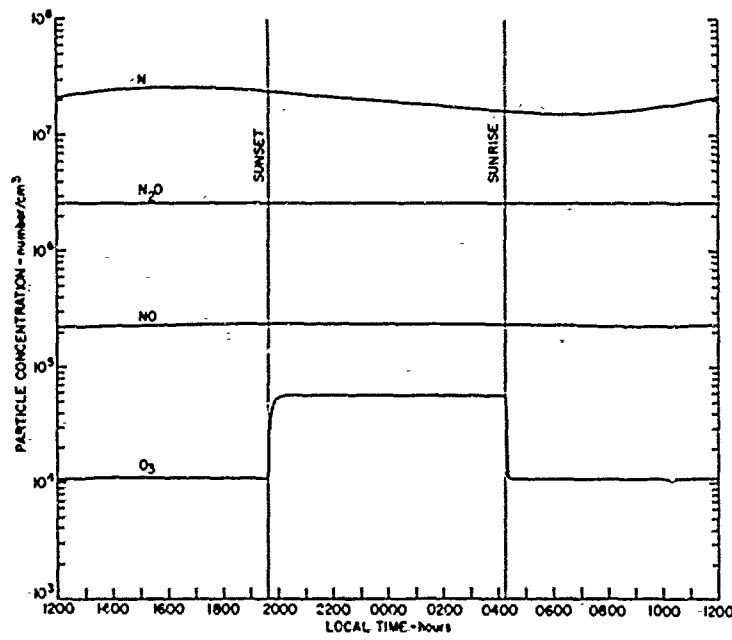


Figure 20. Diurnal Variation of Neutral Species at 110 km (Brazil noontime)



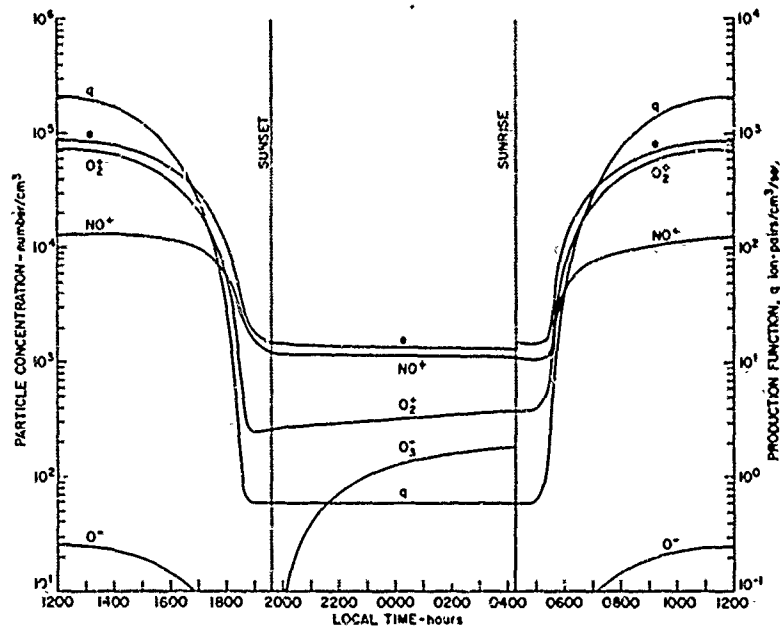


Figure 21. Diurnal Variation of Charged Species at 100 km (Brazil noontime).

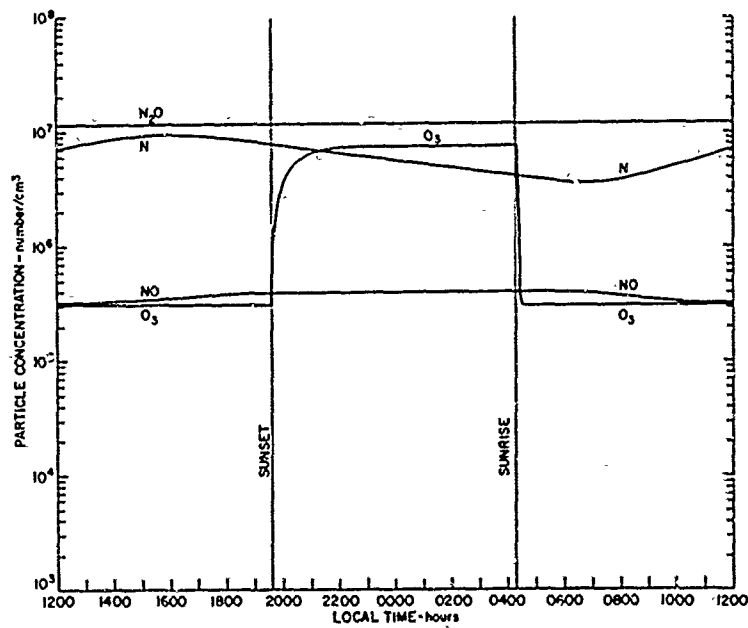


Figure 22. Diurnal Variation of Neutral Species at 100 km (Brazil noontime)

a greater diurnal variation in ozone. Below 100 km the major source of ozone is the three-body recombination reaction  $O + O_2 + M \rightarrow O_3 + M$ . When photo-dissociation stops at sunset the ozone concentration increases because of this recombination. The time constant for removal of ozone by the neutral rearrangement reaction  $O + O_3 \rightarrow 2O_2$  is about one hour. After this time, therefore, the ozone goes into equilibrium which is established by these two processes.

At 90 km the diurnal variation of the charged species starts to show a behavior different from that at higher altitudes (see Figure 23). The production function no longer shows the smooth decay representative of the absorption of ultraviolet radiation. Around 90 km during the day, the primary source of ionization is the soft X-rays with the UV radiation almost completely absorbed above this altitude. As the solar zenith angle increases, more and more of these X-rays are absorbed because of the increasing air mass in the column. The  $L_{\alpha}$  radiation, however, suffers less absorption in the column as the solar zenith angle increases. A point is reached, therefore, where the incident X-ray flux becomes less than the incident  $L_{\alpha}$  flux. This change over to  $L_{\alpha}$  production is evidenced by the bumps in the production curve in Figure 18 around 1800 and 0600 hours. At this altitude during the day  $O_2^+$  is still the major positive ion and the electrons are still lost by recombination. During the night, however, the rate of electron removal by recombination becomes relatively small because of the low electron density. The process that starts to become important at this altitude is the three-body attachment  $O_2 + e + O_2 \rightarrow O_2^- + O_2$ . During the night, therefore, the electrons are lost by attachment to  $O_2$ . The  $O_2^-$  ions thus formed do not stay around very long because the rate of the charge transfer reaction  $O_2^- + O_3 \rightarrow O_3^- + O_2$  is increasing rapidly with the increasing ozone concentration. As soon as the  $O_2^-$  ions are formed they immediately transfer their charge to ozone forming  $O_3^-$  ions. The  $O_3^-$  ions increase until an equilibrium is established between the charge transfer and the mutual neutralization reaction  $O_3^- + NO^+ \rightarrow O_3 + NO$ . As soon as the sun starts to rise, the electrons are detached from the  $O_3^-$  ions and in a few seconds all of the electrons that were attached during the night are detached. Because the solar radiation must penetrate very dense air columns just after sunrise, the production function does not become effective in producing ionization for about an hour after the sun has come up. During this period of time, with no source of ionization present, the electrons recombine with the positive ions, causing the ionization to start to decay. When the production function becomes effective in producing ionization, the electron and positive ion concentrations start to increase and proceed to their noontime equilibrium values.

The diurnal variation of the minor neutral species at 90 km is shown in Figure 24. The behavior at this altitude is similar to that at 100 km. The ozone concentration displays a greater diurnal variation at this altitude because of the increase in the rate of the three-body recombination.

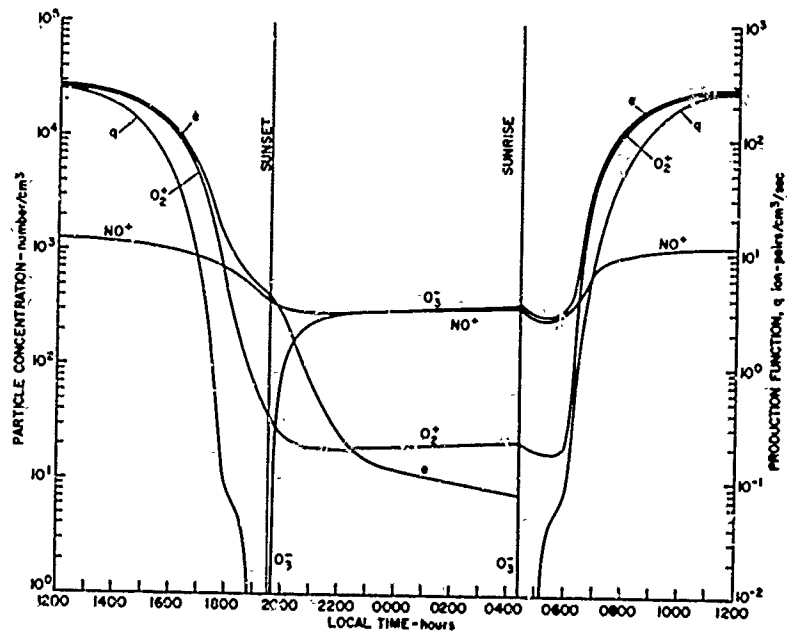


Figure 23. Diurnal Variation of Charged Species at 90 km (Brazil noontime)

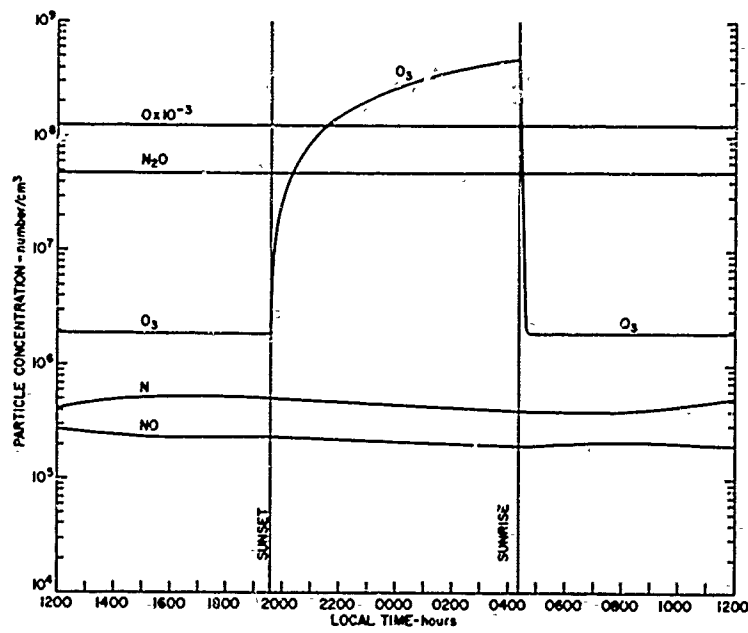


Figure 24. Diurnal Variation of Neutral Species at 90 km (Brazil noontime)

The diurnal variation of the major charged species at 80 km is shown in Figure 25. The daytime ionization picture is now changing considerably. The major positive ion during the entire day is  $\text{NO}^+$ . The  $\text{O}_2^+$  concentration is about two orders of magnitude below the  $\text{NO}^+$  concentration. The electrons and positive ions decay during the afternoon by recombination. The  $\text{O}_2^-$  density follows the electron concentration because of quasi-equilibrium established between the three-body attachment and the photodetachment. The  $\text{O}_3^-$  concentration follows the other negative ions because of the equilibrium between the charge transfer  $\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2$  and the photodetachment. As soon as the sun starts to set, the electrons become attached to  $\text{O}_2$ . This attachment continues until the rate of removal is balanced by the rate of formation by the source function. At this altitude also the  $\text{O}_2^-$  ions formed by electron attachment are short-lived, transferring their charge to ozone to form the  $\text{O}_3^-$  ions. When the dissociative recombination of  $\text{NO}^+$  stops at sunset because of the decreased electron density, the  $\text{NO}^+$  concentration increases by the nighttime production function until a quasi-equilibrium is established between  $\text{O}_3^-$  and  $\text{NO}^+$  as determined by the nighttime source and the time constant of the mutual neutralization process  $\text{O}_3^- + \text{NO}^+ \rightarrow \text{O}_3 + \text{NO}$ . The electron concentration decays slowly throughout the night because of attachment to  $\text{O}_2$ . The resulting  $\text{O}_2^-$  ions thus formed immediately transfer their charge to ozone to form  $\text{O}_3^-$  ions. The behavior of the ionization after sunrise is the same as at 90 km except that three-body attachment and negative charge transfer start to bring negative ions into the picture.

Figure 26 shows the diurnal variation of the minor neutral species at 80 km where again there is the large diurnal variation in ozone. Atomic oxygen is now starting to show a diurnal variation also. The atomic-nitrogen behavior is quite different from what it was at higher altitudes. Below 80 km its kinetics are determined solely by neutral reactions. When the sun sets the photodissociation of  $\text{N}_2\text{O}$  stops thus halting the production of N atoms. With no other source of production present for these atoms, they decay during the night by the neutral rearrangement process  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . After sunrise the concentration of this atom increases until an equilibrium is established between the photodissociation of  $\text{N}_2\text{O}$  and the neutral rearrangement.

The diurnal variation of the charged species at 70 km is shown in Figure 27. The behavior of the species at this altitude is controlled by the same process as at 90 km. With the values of the rate constants for the photodetachment from  $\text{O}_3^-$  (1.4) and for the charge transfer reaction  $\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2$  ( $7.77 \times 10^{-9}$ ) used in this work a negative ion-to-electron ratio of about unity is obtained at 70 km. The negative ion concentrations are higher here than they are at 80 km because of the higher rate of the three-body attachment reaction which, in turn, results from the higher neutral concentration at 70 km.

Figure 28 shows the diurnal variation of the minor neutral species at 70 km. At this altitude, atomic nitrogen becomes a trace species and is therefore not plotted.

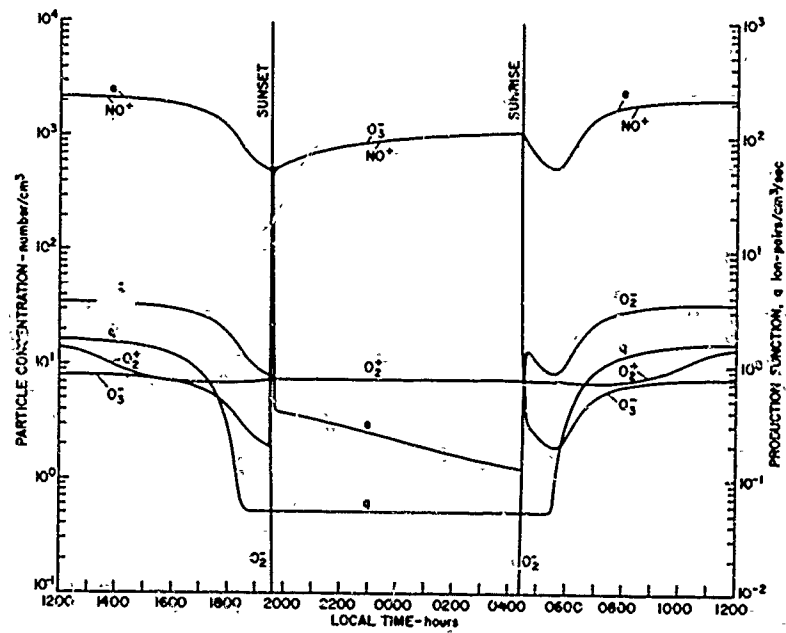


Figure 25. Diurnal Variation of Charged Species at 80 km (Brazil noontime)

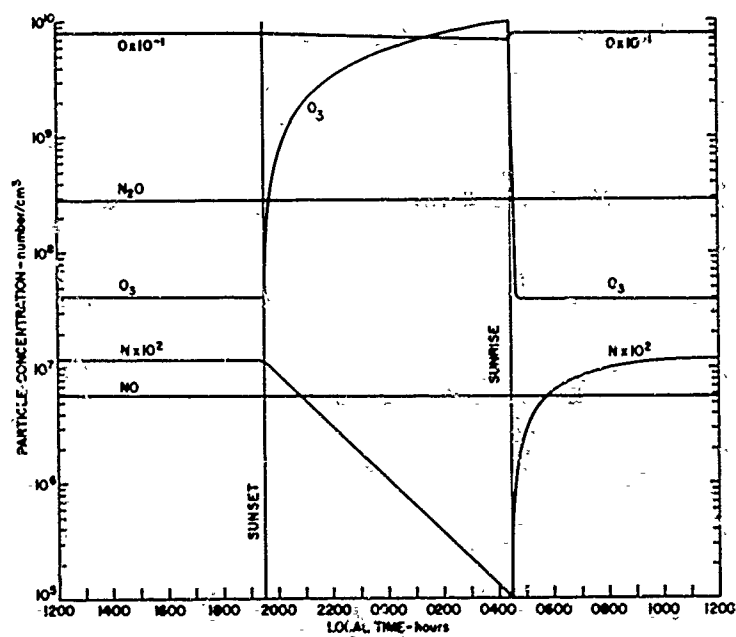


Figure 26. Diurnal Variation of Neutral Species at 80 km (Brazil noontime)

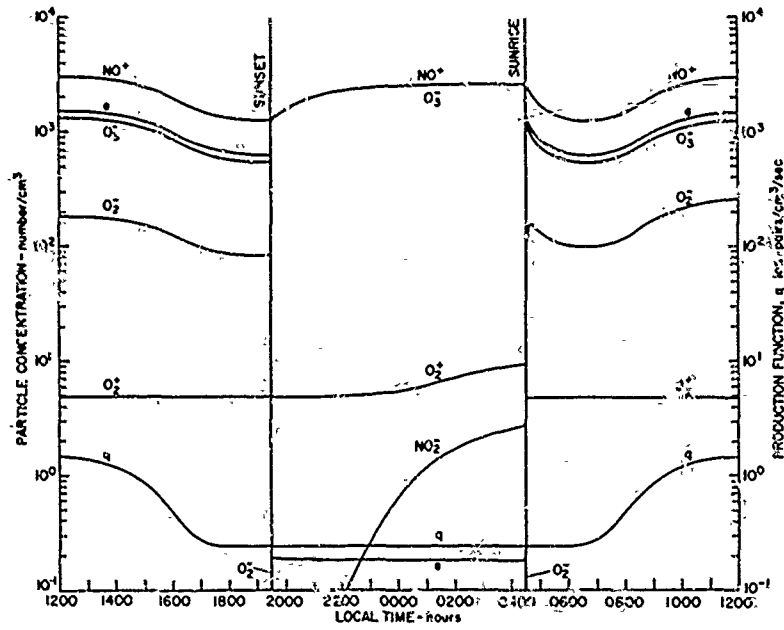


Figure 27. Diurnal Variation of Charged Species at 70 km (Brazil noontime).

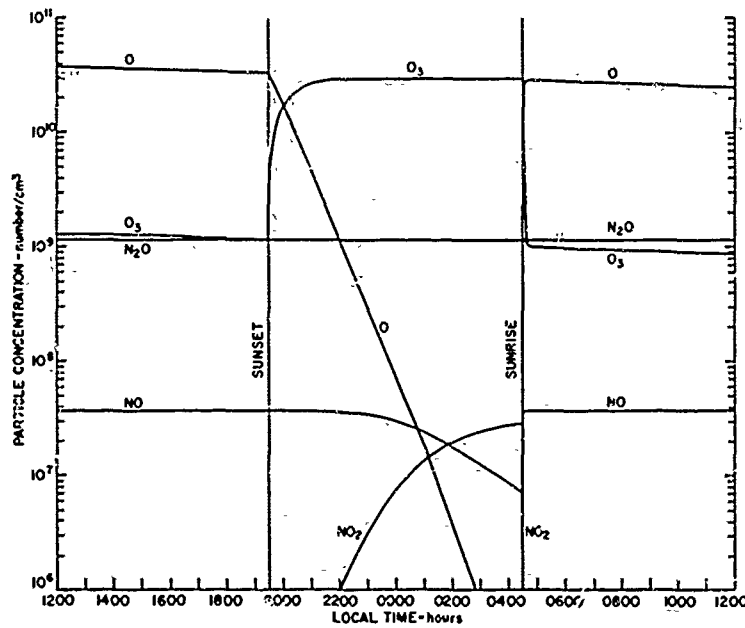


Figure 28. Diurnal Variation of Neutral Species at 70 km (Brazil noontime).

The striking feature of Figure 28 is the considerable diurnal change that takes place in the atomic oxygen concentration. The molecular oxygen and total concentration have become sufficiently high to make the three-body recombination process  $O_2 + O + M \rightarrow O_3 + M$  proceed very rapidly. During the night when there is no photodissociation of ozone to replenish the atomic oxygen supply, the three-body recombination converts practically all of the available oxygen atoms to ozone. When the sun comes up, however, the photodissociation of ozone is so rapid that the oxygen atoms that recombined during the night are restored in a few minutes. The nitric oxide concentration also exhibits a substantial diurnal change at 70 km. The neutral rearrangement reaction  $O + NO_2 \rightarrow NO + O_2$ , the major formation process for this molecule during the day, decreases in effectiveness as the atomic oxygen disappears during the night. Since there is no other effective formation process for this molecule, its concentration decreases through the neutral rearrangement reaction  $N + NO \rightarrow N_2 + O$ .

The nitric oxide concentration returns quickly to its daytime level when the sun rises and the atomic oxygen is restored. Nitrogen dioxide is an extremely minor species down to 70 km. At this altitude it exhibits a sufficient diurnal variation so that by the end of the night it is almost equal in concentration to the nitric oxide. The concentration of this molecule is controlled by its photodissociation and the three-body recombination reaction  $O + NO + M \rightarrow NO_2 + M$ . During the night when there is no photodissociation, the concentration of this molecule increases by the three-body atom recombination. When the sun comes up, the nitrogen dioxide is dissociated very rapidly.

The diurnal variation of the major charged species at 60 km is shown in Figure 29. Because there is no change in the production function throughout the day and because the time constant for recombination is long, there is little change in the electron and  $NO^+$  concentration during the afternoon. The diurnal variation solution at 60 km should have been run over another diurnal cycle. It is apparent that the concentrations at the beginning and at the end of the solution shown in Figure 29 do not coincide sufficiently well. Nevertheless,  $O_3^-$  is the most abundant negative species throughout the entire day. During the night the  $NO_2^-$  ion, which was a trace ion at all altitudes above 60 km, becomes the second most abundant negative species. This ion follows the nitrogen dioxide profile shown in Figure 30 since it is formed by the charge transfer  $O_3^- + NO_2 \rightarrow NO_2^- + O_3$ . When the sun comes up and the concentration of  $NO_2$  decreases again, the  $NO_2^-$  ions transfer their charge back to ozone,  $NO_2^- + O_3 \rightarrow O_3^- + NO_2$ .

Figure 30 shows the diurnal variation of the minor neutral species at 60 km. The ozone still undergoes a diurnal variation but the magnitude of the variation is less at 60 km because there is less atomic oxygen available to produce it. Within about an hour after sunset practically all of the atomic oxygen has recombined.

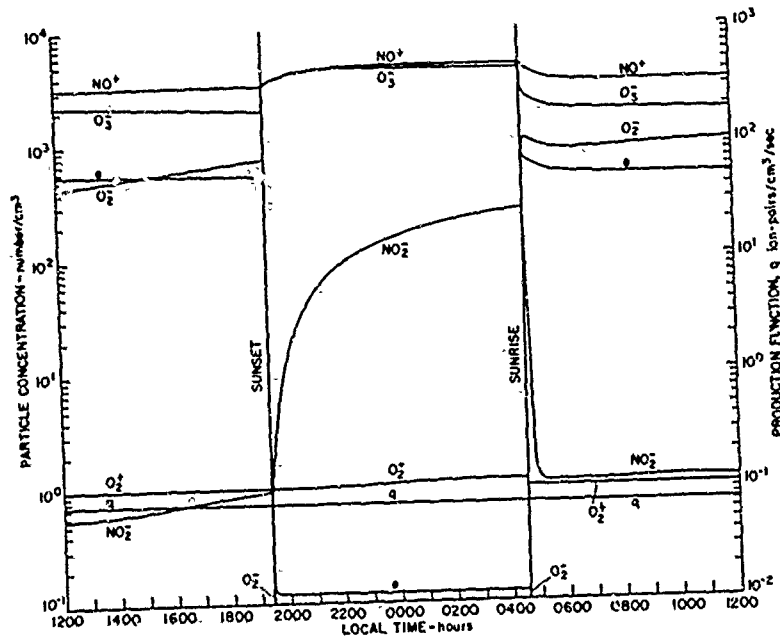


Figure 29. Diurnal Variation of Charged Species at 60 km (Brazil noontime)

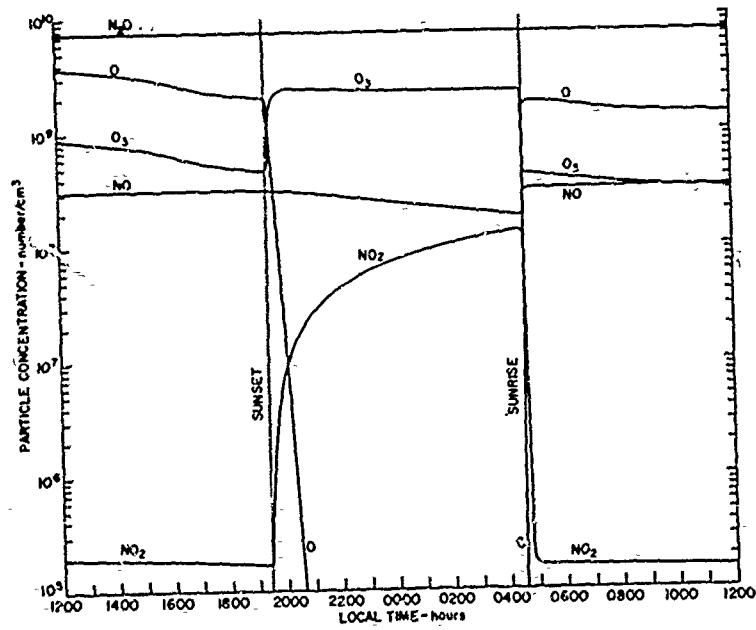


Figure 30. Diurnal Variation of Neutral Species at 60 km (Brazil noontime)



The nitrogen dioxide concentration again exhibits a large diurnal variation arriving at a concentration almost equal to that of nitric oxide at sunrise. The nitric oxide undergoes a lesser variation at 60 km than it did at 70 km because the formation of this molecule stops when the atomic oxygen becomes depleted. Its removal by the neutral rearrangement reaction  $N + NO \rightarrow N_2 + O$  is then much slower because of the greatly reduced atomic nitrogen concentration.

### 5.3.3 VERTICAL PROFILES OF THE SPECIES

In order to obtain a composite picture of the curves discussed in Section 5.3.2, the concentrations of the species were plotted as a function of altitude for noontime and midnight. Figure 31 shows the vertical profile of the charged species at noontime. The electrons remain the most abundant negative species down to 70 km. Below this altitude  $O_3^-$  becomes the most abundant negative species. Above 90 km  $O_2^+$  is the most abundant positive ion. Between 80 and 90 km  $NO^+$  replaces  $O_2^+$  as the most abundant positive ion and remains so at all altitudes below 80 km. Nowhere are  $O^+$ ,  $N_2^+$ ,  $O^-$ , and  $O_2^-$  important ions. In the lower D region  $O_2^-$  becomes important.

The vertical distribution of the neutral species at noontime is shown in Figure 32. The NO profile remains fairly constant down to 90 km while below this altitude it increases steadily with decreasing altitude. The ozone profile appears to have a maximum around 70 km. Above this altitude it falls off rapidly to a very minor constituent. The  $N_2O$  concentration increases with decreasing altitude throughout the entire range. Atomic nitrogen appears to have a peak in the E region around 110 km and becomes a very minor species in the D region. The atomic oxygen profile is that obtained by the chemistry after the second diurnal variation cycle. In this time atomic oxygen has not gone into chemical equilibrium in the E region. Several more diurnal cycles would have had to be made to obtain this equilibrium. The dashed curve is the initial profile assumed for atomic oxygen.

Figure 33 shows the vertical profile of the charged species at midnight. The distribution is considerably different from that shown in Figure 31 for noontime. The electrons remain the most abundant negative species in the E region. Below 95 km, however,  $O_3^-$  is the most abundant negative species. At all altitudes  $NO^+$  is the predominant positive ion. No other ion is important except for  $O_2^+$  in the E region and  $NO_2^-$  at 60 km.

The height profiles for the neutral species at midnight are shown in Figure 34. There is little change in the profile of atomic oxygen down to 80 km but below this altitude it suffers a severe diurnal variation. The ozone profile has shifted to higher concentrations by a little more than an order of magnitude. This reflects the increased production of this molecule during the night by the three-body atom recombination reaction. Atomic nitrogen varies little above 90 km but below this

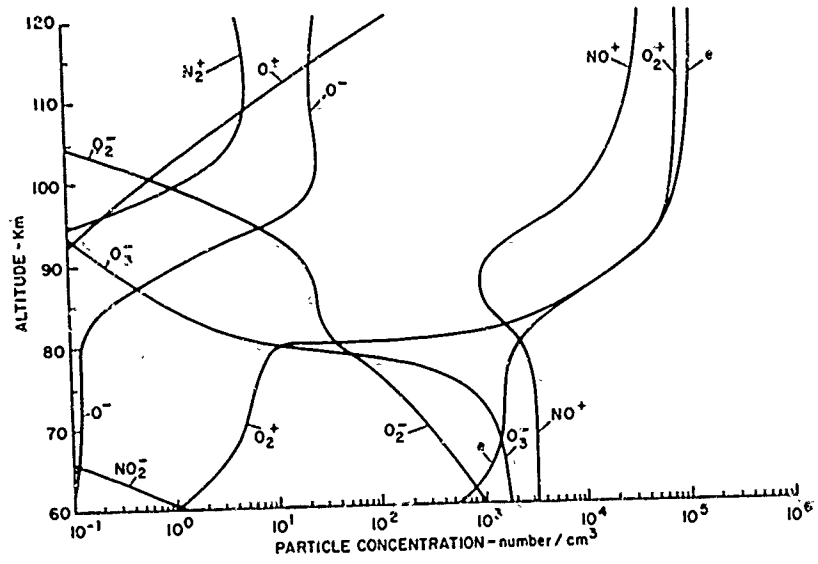


Figure 31. Vertical Distribution of Charged Species (Brazil noontime)

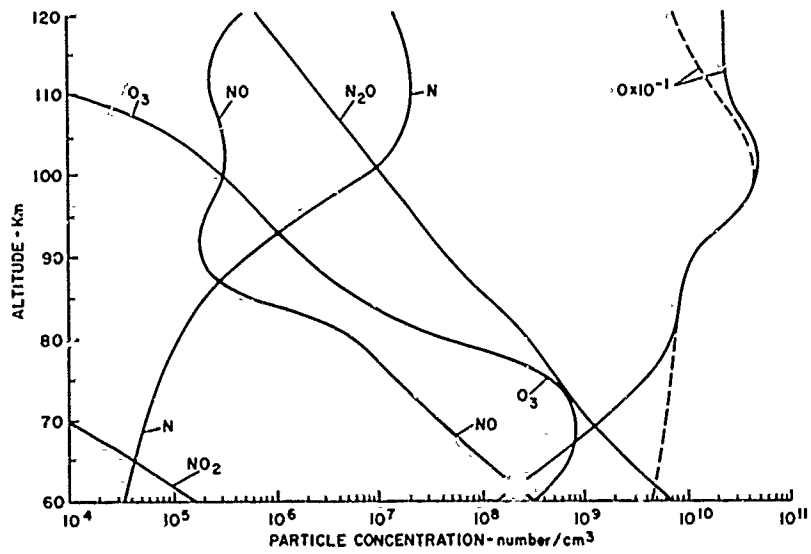


Figure 32. Vertical Distribution of Neutral Species (Brazil noontime)

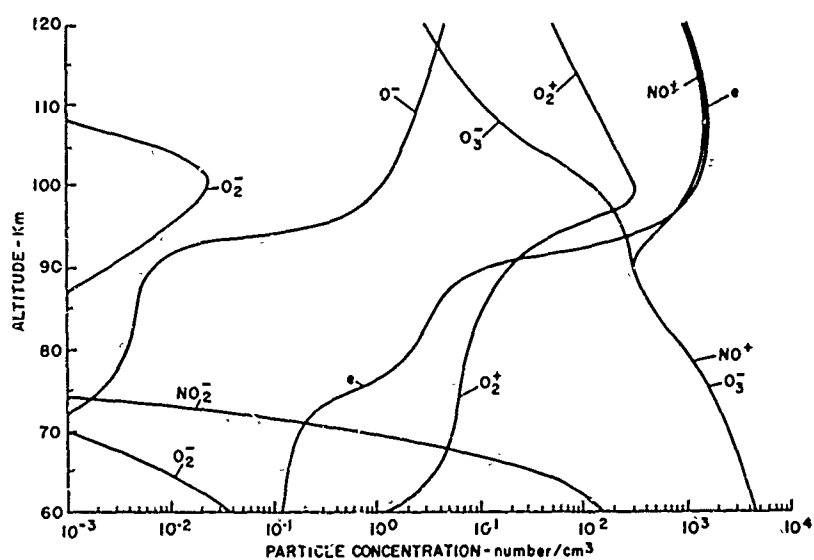


Figure 33. Vertical Distribution of Charged Species (Brazil midnight)

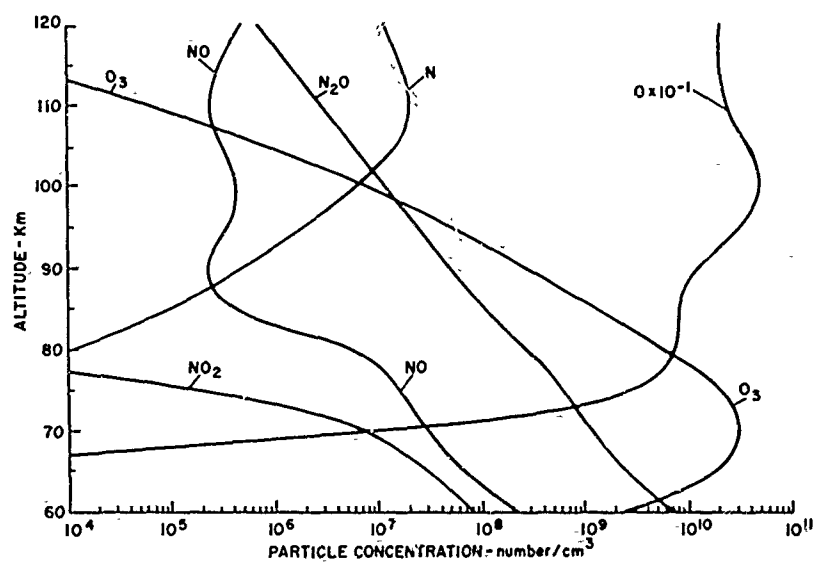


Figure 34. Vertical Distribution of Neutral Species (Brazil midnight)

altitude it undergoes considerable diurnal change. The nitric oxide and the nitrogen peroxide profiles show very little change from noontime to midnight. The nitrogen dioxide concentration is much higher at midnight than at noontime below 80 km, again showing diurnal variation.

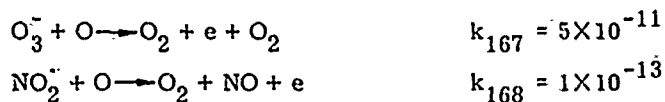
## 6. DISCUSSION OF THE CODE

### 6.1 Example of How Experimental Evidence is Used to Adjust Rate Constants

It would be interesting at this point to present one example of a solution using rate constants for some reactions different from those already discussed. This will demonstrate how the code can be used to detect discrepancies in the values of rate constants or deficiencies in the chemistry. Figure 35 shows a diurnal variation solution at 70 km using the same code that produced Figure 27. The only differences between the two runs are the values of two rate constants and the inclusion of two additional reactions. The two reactions whose rate constants are changed are



These are the rate constants listed in the basic list in Section 3 as compared to 1.4 and  $7.77 \times 10^{-9}$  respectively, used for the diurnal variation calculations. The two additional reactions are



The two rate constant changes have the effect of slowing down both of the reactions. The rate constants for these four reactions are the same as those used to compute the deionization profiles in Section 4.

Since fewer  $\text{O}_2^-$  ions are losing their charge to ozone, the second largest negative species in Figure 35 is  $\text{O}_2^-$  whereas in Figure 27 it is  $\text{O}_3^-$ . Otherwise the behavior of the charged species during the day is much the same in both Figures 27 and 35. During the night, however, the behavior is quite different. The rapid decay of the electrons by attachment to  $\text{O}_2$  and of the  $\text{O}_2^-$  ions by charge transfer to ozone as seen in Figure 27 does not take place in Figure 35, although the electrons still attach to  $\text{O}_2$  to form  $\text{O}_2^-$ . In this computation the

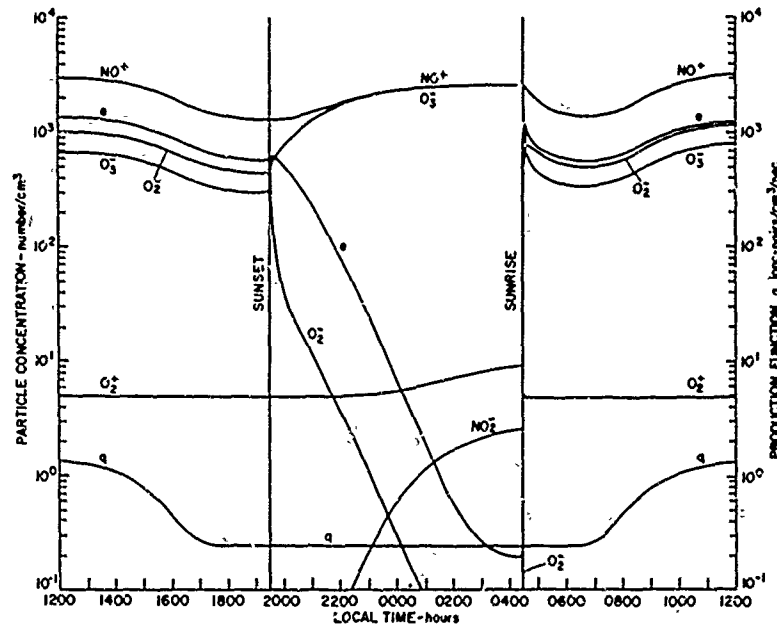


Figure 35. Diurnal Variation of Charged Species at 70 km Using Different Reaction Rates

associative detachment reaction  $O_3^- + O \rightarrow 2O_2 + e$  is the fastest process in the kinetics, so that the electrons consumed by attachment are immediately restored. Since the associative detachment reaction is the controlling process for the electrons, the electron density is determined solely by the behavior of  $O_3^-$  and atomic oxygen. Accordingly, during the night the electron concentration decays slowly along with the atomic oxygen concentration. In this run the atomic-oxygen profile is the same as that shown in Figure 28. Since the  $O_2^-$  density goes into quasi-equilibrium with the electrons shortly after sunset, it decays during the night at a constant ratio to the electron density.

It is obvious that this nighttime behavior is contrary to all experimental evidence where the electrons do decay rapidly after sunset at this altitude. Some of the conclusions that can be drawn are the following:

- The associative detachment reaction  $O_3^- + O \rightarrow 2O_2 + e$  either does not take place or it has an extremely small rate constant.
- There is some chemical reaction missing that is faster than the associative detachment for the removal of  $O_3^-$  and which does not produce electrons.
- Atomic oxygen recombines much more rapidly than it does in this solution so that the associative detachment reaction becomes ineffective much sooner after sunset.

Bortner (1966) stated that the products of the associative detachment reaction are most probably not  $O_2$  and an electron but  $O_2$  and  $O_2^-$  and that the reaction has a rate constant of about  $1.4 \times 10^{-10}$ . If this is the case the negative ion picture will certainly be different and the strange behavior of the electrons, as shown in Figure 35, will be eliminated.

## 6.2 Recommendations

It can be assumed that the complete chemical behavior of the atmospheric constituents is not contained in the long list of reactions built into the code. Not only could significant chemical processes be missing but also important constituents may be omitted. For example, it is possible that the  $NO_2^+$  ion is an important charged species. In work recently presented by Fehsenfeld et al. (1966), they have indicated that the ions  $CO_3^-$  and  $NO_3^-$  might be important. Narcisi (1965) detected the presence in the ionosphere of metallic ions as well as water vapor and its derivative molecular ions. Therefore, it is evident that the chemical make-up of the ionosphere has not been completely defined. As new information becomes available on the presence of any particular species in the ionosphere, the code will have to be updated to include this species as soon as reasonable chemistry for its kinetics can be determined. The code on the other hand is written so that it can accommodate such additions with almost no effort.

It should be pointed out that more information is needed on some of the reaction rates. For application to the sunrise problem, for instance, it is essential that work be done to determine the spectral dependence of the photodetachment of the important negative ions as well as the spectral dependence of the photodissociation of the important minor neutral molecules. Since the code produces results that are only as good as our knowledge of the rate constants of the reactions, laboratory measurements of the important processes not yet studied must be undertaken. Another serious deficiency is the almost complete lack of insitu data on the identification of the most abundant negative ion in the D region. Until experimentalists have determined which ion this is it will be difficult to improve the chemistry of the D region.

As more data become available the code should be able to produce profiles that are more in conformity with experimental measurements and thereby increase its potential as a prediction technique. Meanwhile, the code remains a powerful tool for investigating complicated ionospheric phenomena that cannot be adequately explained by simpler means.

All of the solutions discussed in this paper were obtained using the code as described in Section 7. This code was written to compute only the photochemical behavior of the atmospheric constituents. It does not pretend to be able to solve the complete dynamical problem. To make the code completely general such

physical phenomena as diffusion, turbulent mixing, or eddy diffusion and wind motions and shears must necessarily be included. It is conceivable that none of these dynamic forces are of great importance to the behavior of the charged species incorporated into the present code because of the short time constants of the important chemical reactions. For the neutral species, however, these transport mechanisms can be significant especially if any of these motions have time constants shorter than the time constants of the important chemical processes. From the work that Colgrove, Johnson, and Hanson (1966) have done on the eddy diffusion of atomic oxygen, it is obvious that the problem of mixing cannot be ignored.

For most applications the transport problems are of minor importance. Therefore, it is not intended at the present time to extend the code in this direction. For certain minor neutral species it might become necessary to establish initial conditions by taking vertical transport into account. However, it is anticipated that this might be accomplished satisfactorily by a semi-empirical approach.

## 7. DESCRIPTION OF THE CODE

The code consists of a main program and several subroutines all written in FORTRAN-IV language for an IBM-7044 computer. Application of the code to any FORTRAN-compatible computer is easily made. The basic program package consists of the following programs:

- |                     |                       |
|---------------------|-----------------------|
| a) Main program     | f) Subroutine INITIAL |
| b) Subroutine INTEG | g) Subroutine PRODUC  |
| c) Subroutine ALGA  | h) Subroutine BALAN   |
| d) Subroutine SLOP  | i) Subroutine DAUXT   |
| e) Subroutine DAUX  |                       |

### 7.1 Ionization Codes

Two of the simpler problems to which the code can be applied are the buildup of ionization under the influence of a constant or variable source of ionization and the decay of ionization from some initial values with or without an external source of ionization. The results presented in Section 4 were obtained using the code as described here.

#### 7.1.1 MAIN PROGRAM RATEQ

The functions of the main program are to fix a standard set of rate constants in DATA statements to control the input of necessary parameters and the output of results, to initialize the entire code before starting a solution, to monitor the flow of the computations, and to determine the equilibrium status of the species.

### 7.1.1.1 The Rate Constants

In order to avoid reading the rate constants into the computer for every run, a standard set of rate constants was built into the code. These rate constants are listed in Section 3. Every rate constant is considered to be of the form

$$k = A \cdot T^B \cdot e^{-C/T} \quad (39)$$

where A, B, and C are constants and T is the temperature in degrees Kelvin. The constants A are set into regions A1(69), A2(69), and A3(30). This split up is necessary because of the restriction on the number of CONTINUATION cards allowed by the version of FORTRAN that is used. The B's and C's are set into regions B(168) and C(168) respectively. After the temperature and any required changes in the rate constants are read into the computer, the actual rate constants are computed from Eq. (39) and put into the CON region.

### 7.1.1.2 Determination of Equilibrium

The decision as to whether a species has reached its equilibrium or quasi-equilibrium value is made by the main program. For this purpose the four regions LOCK (15), KEY(15), CRTNO(15), and CRITN(15) are used. Upon completion of an integration, the values

$$\text{CRTNO}(J) = N_j \sum R_i \quad (40)$$

and

$$\text{CRITN}(J) = \frac{\Delta N_j}{\Delta t} \quad (41)$$

are computed. If the slopes  $\frac{\Delta N_j}{\Delta t}$  are less than  $10^{-3}$ , the criterion for quasi-equilibrium is

$$\left| 1 - \frac{\sum F_i}{N_j \sum R_i} \right| < \text{DEL} \quad (42)$$

If the slopes  $\frac{\Delta N_j}{\Delta t}$  are greater than  $10^{-3}$ , the criterion for quasi-equilibrium is



$$\frac{\left| \frac{\Delta N_j}{\Delta t} \right|}{N_j \sum R_i} < DEL \quad (43)$$

The equilibrium status of each species is determined by using that criterion which pertains.

If the criterion fails for any species, the respective LOCK(J) is set to zero. If the test is satisfied, a one is added to the respective LOCK(J). After the criterion is tested for all the species, the LOCK(15) are tested to determine if any have reached three. If a particular LOCK(J) is equal to or greater than three, the respective KEY(J) is set to two. Following this another test is made to determine if any species has decayed below the value CHI. If any one has, the respective KEY(J) is set equal to three. Once a KEY(J) is set to three it will remain at that value for the remainder of the solution. The values in the KEY region are used by several of the subroutines for branching, depending on the status of the concentrations of the species.

The status of any particular species can be determined at any time by simply investigating its KEY value. The species j will not be in equilibrium if its KEY is on one; it will be in equilibrium if its KEY is on two; its concentration will be zero or a constant; its equations are removed from the sets if its KEY is on three; and, its concentration will be computed from the charge balance equation.

$$\sum N_- = \sum N_+ \quad (44)$$

if its KEY is on four.

#### 7.1.1.3 Input Parameters

Those parameters that the code requires to solve a specific problem are put on cards that immediately follow the binary decks for the program. The binary decks and the BCD data cards are read into the computer from FORTRAN-tape 5. The purpose of each data card and the FORMAT in which it is prepared are as follows:

- |        |   |
|--------|---|
| CARD 1 | FORMAT(12A6)<br>This card contains up to 70 BCD characters that can be used for identification at the discretion of the user. |
| CARD 2 | FORMAT(1P4E12.5)<br>This card contains four variables:  |

- (1) EUBAR - the criterion for the solution in the integrating routine. This must be some number less than  $10^{-2}$  which is determined only by the degree of accuracy desired in the integrated values.
- (2) ELBAR - the criterion for the solution of the exponential equations. This must be some number less than  $10^{-3}$  which is determined by the amount of charge imbalance that can be tolerated in the results.
- (3) DEL - the criterion for equilibrium. This should be some number around  $10^{-2}$ . If it is much larger than this, a species will be put into quasi-equilibrium too soon and the solution of the exponential equations can fail. If it is much smaller than  $10^{-2}$  and a species is in equilibrium, its differential equation may not be removed from the set. The set of differential equations cannot be solved with the current increment if the set contains an equation for a species whose concentration is in equilibrium or quasi-equilibrium. In order to solve such a set of equations, the increment will have to be reduced considerably at the expense of much computer time.
- (4) ENDT - the time in seconds to which the solution is to run. This is the time associated with  $dN/dt$  and is not to be confused with the running time of the code on the computer.

CARD 3

FORMAT(I4)

This card contains the integer NOC indicating the number of rate constants that are to be changed for the run. If no changes are necessary, this card must contain a zero. Following this card are the changes themselves. If there are no changes, CARD 4 is read next. The changes are punched one per card in FORMAT(I4,1PE10.2,OPF5.1,1PE10.2,7A6). Field 1 is the reaction number as listed in Section 3, fields 2, 3, and 4 are the A, B, and C in Eq. (39), field 6 represents any 42-BCD characters that the user wishes to insert as comments.

## CARD 4      FORMAT(1P5E12, 5)

This card contains five input parameters:

- (1) ALT - the altitude in centimeters at which the solution is to be made.
- (2) D - the total number density in  $\text{cm}^{-3}$ .
- (3) DO2 - the concentration of molecular oxygen in  $\text{cm}^{-3}$  at the given altitude.
- (4) DN2 - the concentration of molecular nitrogen in  $\text{cm}^{-3}$  at the given altitude.
- (5) T - the temperature in degrees Kelvin at the given altitude.

## CARDS 5-7    FORMAT(1P6E12, 5)

These cards contain the initial concentrations of the species in the following order: electrons,  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{N}_2^+$ ,  $\text{NO}^+$ , NO, N,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , and atomic oxygen. The last value in this set is the constant production rate in number of ion-pairs/ $\text{cm}^3/\text{sec}$ .

## CARD 8      FORMAT(4I2)

This card contains the option switches.

KB1=0 for logarithmic output.

KB1=1 for decimal output.

KB2=0 calls DAUXT to print the history of the reactions.

KB2=1 suppresses the call of DAUXT.

KB3=0 prints this history after every integration if DAUXT is called.

KB3=1 prints this history only once for each decade of time if DAUXT is called.

KB4=0 returns control to the system on an error.

KB4=1 program returns to the input area to read another set of data cards when an error occurs.

It is possible to stack as many sets of these data cards as desired because the program always returns to the input area when it has completed the computations for a given set of data.

## 7.1.1.4 Programmed Variables

There are other parameters that can be changed by reassembly of the main program:

- a) CHI - the lowest value to which a species may decay. This test is incorporated to prevent computer underflow in the event that any species concentration decays below  $10^{-38}$ . The limiting value used in the programs given here is  $10^{-10}$ . If a species should try to decay below this value, its concentration is set to zero and its equations are removed from the sets by setting its KEY on three.
- b) NOCOM - the number of reactions built into the system.
- c) ENLE - a preset lower limit on the electron density. This test is included in order to terminate the solution when the electron density falls below a certain value. This permits the computation of densities only over the range of interest. When the electron concentration decays below this value, control is transferred to the input area of the code. If no limit is to be placed on the electron density, this value must be set to zero.
- d) ITER - the maximum number of iterations that will be made in attempting to solve the simultaneous exponential equations. If a solution cannot be found within this number of iterations, iteration of the exponential equations will stop and the unsuccessful return from subroutine ALGA will be taken.
- e) NUMB - the number of differential equations in the set to be solved.

#### 7.1.1.5 Output

FORTTRAN-tape 6 is the normal system output tape. When the computations are completed, this tape will contain all of the output information with the exception of the history of the reactions. The first thing written on this tape is the comment read into the computer on the first data card. This card contains any 72 hollerith characters that the user wishes to insert as identification. Following this the program writes the list of changes that are made in the build-in standard list of reaction-rate constants. The program then writes the altitude at which the calculations are being made, the total number density, and the temperature. After this is written, the rate constants for the reactions with the coefficient A first and underneath this the total reaction rate with the proper temperature dependence. Following this is the time and the computed concentrations for this time of all the the-negative and the positive-species.

During the execution of the program the time, the concentrations of the neutral species computed for this time, the value of the production function, and the setting of the KEY switches are written on Tape 1 in binary. Upon completion of the solution

for a particular set of input data, this information is automatically transferred to Tape 6. Tape 1 is left in a rewind condition.

FORTRAN-tape 4 is used by subroutine DAUXT for writing the history of the reactions if such a history is requested. Upon completion of the computations, this tape must be removed for off-line printing.

The following statements, beginning on page 72, are a listing of the main program.

#### 7.1.2 THE INTEGRATING SUBROUTING INTEG

This subprogram is called by the main program and performs the numerical integration of the differential equations. For solving a set of differential equations

$$\frac{dN_1}{dt} = F_1(t, N_1, N_2, N_3 \dots N_m) ,$$

$$\frac{dN_2}{dt} = F_2(t, N_1, N_2, N_3 \dots N_m) ,$$

$$\frac{dN_3}{dt} = F_3(t, N_1, N_2, N_3 \dots N_m) ,$$

·  
·

$$\frac{dN_m}{dt} = F_m(t, N_1, N_2, N_3 \dots N_m) .$$

The Kutta Merson solution uses the equations

$$N_{j1} = N_{j0} + \frac{1}{3} \Delta t F_j(t_0, N_{10}, N_{20}, N_{30} \dots N_{m0})$$

$$N_{j2} = N_{j0} + \frac{1}{6} \Delta t F_j(t_0, N_{10}, N_{20}, N_{30} \dots N_{m0}) \\ + \frac{1}{6} \Delta t F_j(t_0 + \frac{1}{3} \Delta t, N_{11}, N_{21}, N_{31} \dots N_{m1})$$

$$N_{j3} = N_{j0} + \frac{1}{8} \Delta t F_j(t_0, N_{10}, N_{20}, N_{30} \dots N_{m0}) \\ + \frac{3}{8} \Delta t F_j(t_0 + \frac{1}{3} \Delta t, N_{12}, N_{22}, N_{32} \dots N_{m2})$$

```

$IBFTC RATEQS LIST
C SOLUTION OF THE REACTION RATE EQUATIONS IN THE IONOSPHERE FOR 15 SPERATE000
C IES AND WITH 168 REACTIONS. RATE0005
C KB1=0 FOR LOG OUTPUT. RATE0010
C KB1=1 FOR DECIMAL OUTPUT RATE0015
C KB2=0 PRINTS THE HISTORY OF THE REACTIONS. RATE0020
C KB2=1 REACTION HISTORY NOT COMPUTED. RATE0025
C KB3=0 PRINTS HISTORY AFTER EACH INTEGRATION. RATE0030
C KB3=1 PRINTS HISTORY ONCE EACH DECADE OF TIME. RATE0035
C KB4=0 HALTS ON ERROR. RATE0040
C KB4=1 READS ANOTHER POINT CARD AFTER AN ERROR. RATE0045
C IPLOT=0 NO PLOTTER TAPE MADE. RATE0050
C IPLOT=1 MAKES A LOG PLOTTER TAPE. RATE0055
C UNITS OF INPUT PARAMETERS ARE CGS. RATE0060
C RATE0065
C RATE0070
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGINRATE0075
1(15) RATE0080
COMMON NUMB,EUBAR,ELBAR,D,DO2,ON2,T,PNE,PNO,PO2,PO,PN2,TOTAL,JACK,RATE0085
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOTRATE0090
20,TOTN RATE0095
COMMON VQ(30),IQ(30),SIGM(30),ITEM
DIMENSION DONT(20),TITLE(12),TTREG(20),CRITN(15),CRTNO(15),A(168),RATE0105
1B(168),C(168),LOCK(15),ALF(7),G(168),A1(69),A2(69),A3(30) RATE0110
DATA A1/ 0.44E+00,1.40E+00,0.04E+00,0.04E+00,9.00E-15,3.60E-16, RATE0115
13.60E-16,1.00E-13,1.00E-13,1.00E-13,1.00E-13,1.00E-13,1.00E-13, RATE0120
21.00E-13,1.00E-13,1.31E-15,1.00E-19,1.00E-17,1.00E-17,1.00E-11, RATE0125
31.00E-11,1.00E-31,1.00E-31,1.40E-31,5.80E-33,1.90E-33,6.00E-28, RATE0130
44.00E-29,0.00E-00,6.00E-05,9.00E-05,1.50E-04,1.00E-24,1.00E-22, RATE0135
51.00E-22,1.00E-22,1.00E-23,2.20E-10,1.00E-12,1.00E-12,1.00E-12, RATE0140
65.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07, RATE0145
75.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07,5.00E-07, RATE0150
85.00E-07,5.00E-07,1.00E-23,1.00E-23,1.00E-23,1.00E-23,1.00E-23, RATE0155
91.00E-23,1.00E-23,1.00E-23,1.00E-23,1.00E-23,1.00E-23,1.00E-11/ RATE0160
DATA A2/ 1.00E-13,1.00E-13,0.00E-00,1.00E-13,1.00E-13,1.00E-13,1.00E-11, RATE0165
11.00E-11,1.00E-13,0.00E-00,1.00E-13,1.00E-13,1.00E-13,1.00E-13, RATE0170
24.00E-11,2.40E-11,0.00E-00,0.00E-00,8.00E-10,1.00E-12,1.00E-10, RATE0175
30.00E-00,5.00E-12,1.00E-09,1.00E-09,1.00E-12,1.00E-09,1.00E-09, RATE0180
41.00E-09,1.00E-09,1.00E-16,1.00E-18,0.00E-00,0.00E-00,0.00E-00, RATE0185
50.00E-00,0.00E-00,1.00E-15,1.00E-29,1.00E-29,0.00E-00,0.00E-00, RATE0190
60.00E-00,0.00E-00,0.00E-00,1.00E-30,1.00E-30,3.00E-12,3.00E-12, RATE0195
73.00E-12,1.00E-11,1.80E-10,1.00E-11,2.50E-10,1.00E-11,1.00E-28, RATE0200
81.00E-34,1.00E-17,1.00E-21,1.00E-21,2.00E-17,1.00E-24,6.40E-17, RATE0205
91.00E-24,1.00E-22,1.00E-22,5.00E-32,2.00E-31,5.00E-32,3.20E-35/ RATE0210
DATA A3/ 2.60E-35,6.50E-34,2.00E-31,2.00E-33,3.00E-33,4.50E-33, RATE0215
13.00E-30,1.00E-33,1.00E-33,0.00E-00,1.10E-10,7.10E-17,3.00E-11, RATE0220
22.00E-10,5.00E-11,5.00E-10,3.00E-16,2.50E-11,2.00E-13,4.00E-12, RATE0225
32.00E-11,8.00E-13,5.00E-06,6.00E-08,3.00E-03,4.08E-07,5.58E-08, RATE0230
45.34E-03,1.00E-13,1.00E-13/ RATE0235
DATA B/4*0.0,3*2.0,16*0.0,3*0.5,3*0.0,3*-1.0,5*-1.5,-0.7,3*0.0,16*RATE0240
1-0.5,11*-1.5,55*0.0,-1.0,10*0.0,3*-0.5,3*0.0,-0.5,3*0.0,-1.0,4*0.0RATE0245
2,1.5,4*0.0,1.5,13*0.0/ RATE0250
DATA C/4*0.0,3*5.1E3,0.0,4.7E3,11*0.0,7.2E3,47*0.0,3E3,2*0.0,1E4,7RATE0255
1*0.0,5E3,37*0.0,2E3,3E3,3*0.0,3.5E3,0.0,5E3,4E3,11*0.0,2*-9E2,2*0.0RATE0260
20,2E4,2*-9E2,0.0,3E3,1E4,0.0,3.75E4,1.9E4,5.3E2,1.4E4,1.35E4,2.8E3RATE0265
3,6.6E3,0.0,7E3,2*0.0,1.2E3,8*0.0/ RATE0270
C RATE0275
C RATE0280
C RATE0285
C RATE0290
INITIALIZATION OF SYSTEM AND INPUT.
REWIND 0

```

```

REWIND 1
REWIND 3
REWIND 8
CHI=1.0E-10
NOCOM=168
NUMB=15
ENDE=0.0
ITER=30
KB6=1
5 WRITE(6,400)
  READ(5,445) (TITLE(N),N=1,12)
  WRITE(6,450) (TITLE(N),N=1,12)
  READ(5,395) EUBAR,ELBAR,DEL,ENDT
  READ(5,420) NOC
  IF(NOC .EQ. 0) GO TO 30
  WRITE(6,490)
  DO 25 J=1,NOC
  READ(5,500) I,G(I),B(I),C(I),(ALF(N),N=1,7)
  IF(I .GT. 69) GO TO 10
  A1(I)=G(I)
  GO TO 20
10 IF(I .GT. 138) GO TO 15
  A2(I-69)=G(I)
  GO TO 20
15 A3(I-138)=G(I)
20 WRITE(6,500) I,G(I),B(I),C(I),(ALF(N),N=1,7)
25 CONTINUE
30 READ(5,395) ALT,DD02,UN2,T
  READ(5,395) (BEGIN(J),J=1,15),PROD
  READ(5,415) KB1,KB2,KB3,KB4,IPL0T
  TIME=1.0E-6
  MOUNT=0
  KNT=0
  JAKE=1
  JACK=1
  LAM=6
  KLOT=0
  DO 35 J=1,150
35 TTREG(J)=0.0
  LINT=((2*NUMB)+4)
  I2NT=((3*NUMB)+4)
  K2NT=((4*NUMB)+4)
  J2NT=((5*NUMB)+4)
  N2NT=((6*NUMB)+4)
  DO 40 J=1,NUMB
  TTREG(J+3)=0.0
  LOCK(J)=0
40 KEY(J)=1
  CALL INITAL
C
C
C
  COMPUTE RATE CONSTANTS IN THE FORM  $K=A*(T**B)*EXP(-C/T)$ 
  K=1
  DO 45 J=1,69
  A(K)=A1(J)
45 K=K+1
  DO 50 J=1,69
  A(K)=A2(J)
50 K=K+1
  RATE0295
  RATE0300
  RATE0305
  RATE0310
  RATE0315
  RATE0320
  RATE0325
  RATE0330
  RATE0335
  RATE0340
  RATE0345
  RATE0350
  RATE0355
  RATE0360
  RATE0365
  RATE0370
  RATE0375
  RATE0380
  RATE0385
  RATE0390
  RATE0395
  RATE0400
  RATE0405
  RATE0410
  RATE0415
  RATE0420
  RATE0425
  RATE0430
  RATE0435
  RATE0440
  RATE0445
  RATE0450
  RATE0455
  RATE0460
  RATE0465
  RATE0470
  RATE0475
  RATE0480
  RATE0485
  RATE0490
  RATE0495
  RATE0500
  RATE0505
  RATE0510
  RATE0515
  RATE0520
  RATE0525
  RATE0530
  RATE0535
  RATE0540
  RATE0545
  RATE0550
  RATE0555
  RATE0560
  RATE0565
  RATE0570
  RATE0575
  RATE0580
  RATE0585

```

```

DD 55 J=1,30
A(K)=A3(J)
55 K=K+1
DD 60 J=1,NOCOM
60 CON(J)=A(J)*(T**B(J))*EXP(-C(J)/T)

PREPARE OUTPUT TAPES AND WRITE RATE CONSTANTS AND INITIAL
CONDITIONS.

WRITE(3,450) (TITLE(M),M=1,12)
WRITE(6,405) ALT,D,T
WRITE(6,480)
IS=1
DD 65 J=1,15
IT=IS+5
WRITE(6,455) (I,A(I),I=IS,IT)
WRITE(6,485) (I,CON(I),I=IS,IT)
IS=IS+6
65 CONTINUE
WRITE(6,515)
DD 70 J=1,13
IT=IS+5
WRITE(6,455) (I,A(I),I=IS,IT)
WRITE(6,485) (I,CON(I),I=IS,IT)
IS=IS+6
70 CONTINUE
WRITE(6,410)
IF(K81 .EQ. 0) GO TO 80
75 WRITE(6,505) (TREG(2), (TREG(J), J=4,12), PROD)
WRITE(1) TREG(2), (TREG(J), J=13,18), DD2, DN2, (KEY(J), J=1,15)
MOUNT=MOUNT+1
GO TO 135
80 M=NUMB+3
DO 95 J=2,M
DEC=TREG(J)
IF(DEC) 360,85,90
85 DDNT(J)=0.0
GO TO 95
90 DDNT(J)=ALOG10(DEC)
95 CONTINUE
IF(DD2 .EQ. 0.0) GO TO 100
DDO2=ALOG10(DD2)
GO TO 105
100 DDD2=0.0
105 IF(DN2 .EQ. 0.0) GO TO 110
DDN2=ALOG10(DN2)
GO TO 115
110 DDN2=0.0
115 IF(PROD) 360,120,125
120 DPROD=0.0
GO TO 130
125 DPROD=ALOG10(PROD)
130 WRITE(6,505) DDNT(2), (DDNT(J), J=4,12), DPROD
WRITE(1) DDNT(2), (DDNT(J), J=13,18), DDO2, DDN2, (KEY(J), J=1,15)
MOUNT=MOUNT+1
135 DO 140 K=1,NUMB
IF(KEY(K)-2) 145,140,140
140 CONTINUE
CALL ALGA

```

```

RATE0590
RATE0595
RATE0600
RATE0605
RATE0610
RATE0615
RATE0620
RATE0625
RATE0630
RATE0635
RATE0640
RATE0645
RATE0650
RATE0655
RATE0660
RATE0665
RATE0670
RATE0675
RATE0680
RATE0685
RATE0690
RATE0695
RATE0700
RATE0705
RATE0710
RATE0715
RATE0720
RATE0725
RATE0730
RATE0735
RATE0740
RATE0745
RATE0750
RATE0755
RATE0760
RATE0765
RATE0770
RATE0775
RATE0780
RATE0785
RATE0790
RATE0795
RATE0800
RATE0805
RATE0810
RATE0815
RATE0820
RATE0825
RATE0830
RATE0835
RATE0840
RATE0845
RATE0850
RATE0855
RATE0860
RATE0865
RATE0870
RATE0875
RATE0880

```



```

TREG(3)=2.0*TREG(3)
TREG(2)=TREG(2)+TREG(3)
GO TO 150
C
C   INTEGRATION OF EQUATIONS STARTS HERE.
C
145 CALL INTEG
150 CALL BALAN
    IF(TREG(3) .NE. 2.0E-6) GO TO 155
    KLOT=KLOT+1
    IF(KLOT .GT. 10) GO TO 160
155 KLOT=0
    GO TO 165
160 PRINT 470
    GO TO 365
C
C   OUTPUT OF RESULTS STARTS HERE.
C
165 IF(KNT .NE. 50) GO TO 170
    WRITE(6,410)
    KNT=0
170 KNT=KNT+1
    IF(KNT .EQ. 0) GO TO 175
    WRITE(6,505) TREG(2), (TREG(J), J=4, 12), TOTAL
    WRITE(1) TREG(2), (TREG(J), J=13, 18), DD2, DN2, (KEY(J), J=1, 15)
    GO TO 210
175 K=NUMB+3
    DO 190 J=2, K
    DEC=TREG(J)
    IF(DEC) 360, 180, 185
180 DONT(J)=0.0
    GO TO 190
185 DONT(J)=ALOG10(DEC)
190 CONTINUE
    DD2=ALOG10(DD2)
    DDN2=ALOG10(DN2)
    IF(TOTAL) 360, 195, 200
195 TOTL=0.0
    GO TO 205
200 TOTL=ALOG10(TOTAL)
205 WRITE(6,505) DONT(2), (DONT(J), J=4, 12), TOTL
    WRITE(1) DONT(2), (DONT(J), J=13, 18), DD2, DDN2, (KEY(J), J=1, 15)
210 MOUNT=MOUNT+1
    CALL PLOT(IPL0T)
    IF(JAKE=2) 215, 350, 355
215 JACK=2
    KIND=1
    CALL SLOP(KIND)
    KIND=2
    CALL SLOP(KIND)
    N2=LINT
    DO 220 I=1, NUMB
    CRITN(I)=2.0*ABS((TREG(N2)-TREG(I+3))/TREG(3))
    CRTNO(I)=REMV(I)*TREG(I+3)
    N2=N2+1
220 CONTINUE
    CRTNO(10)=CRTNO(10)+PNO
    CRTNO(15)=CRTNO(15)+PO
    DO 250 J=1, NUMB
RATE0885
RATE0890
RATE0895
RATE0900
RATE0905
RATE0910
RATE0915
RATE0920
RATE0925
RATE0930
RATE0935
RATE0940
RATE0945
RATE0950
RATE0955
RATE0960
RATE0965
RATE0970
RATE0975
RATE0980
RATE0985
RATE0990
RATE0995
RATE1000
RATE1005
RATE1010
RATE1015
RATE1020
RATE1025
RATE1030
RATE1035
RATE1040
RATE1045
RATE1050
RATE1055
RATE1060
RATE1065
RATE1070
RATE1075
RATE1080
RATE1085
RATE1090
RATE1095
RATE1100
RATE1105
RATE1110
RATE1115
RATE1120
RATE1125
RATE1130
RATE1135
RATE1140
RATE1145
RATE1150
RATE1155
RATE1160
RATE1165
RATE1170
RATE1175

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```

IF(CRITN(J)-1.0E-3) 225,225,230
225 IF(ABS(1.0-(FORM(J)/CRTND(J)))-DEL) 245,245,240
230 IF(CRTND(J)) 235,250,235
235 IF((CRITN(J)/CRTND(J))-DEL) 245,240,240
240 LOCK(J)=0
    GO TO 250
245 LOCK(J)=LOCK(J)+1
250 CONTINUE
255 DO 275 J=1,NUMB
    IF(KEY(J)-3) 260,275,275
260 IF(LOCK(J)-3) 265,270,270
265 KEY(J)=1
    GO TO 275
270 KEY(J)=2
275 CONTINUE
    DO 280 J=1,NUMB
    IF(KEY(J) .GT. 2) GO TO 280
    IF(TREG(J+3) .GT. TTREG(J+3)) GO TO 280
    IF(TREG(J+3) .GT. CHI) GO TO 280
    KEY(J)=3
    TREG(J+3)=0.0
280 CONTINUE
    IF(PNE) 300,285,300
285 IF((TREG(4)/BEGIN(1))-1.0E-3) 290,300,300
290 DO 295 J=1,3
    TREG(J+3)=0.0
295 KEY(J)=3
300 DO 305 J=1,NUMB
305 TTREG(J+3)=TREG(J+3)
    IF(KB2 .EQ. 1) GO TO 315
310 CALL DAUXT
C
C   DECISION TO CONTINUE INTEGRATION-OK STOP IS MADE HERE.
C
315 IF(TREG(4) .LT. ENDE) GO TO 370
    IF(TREG(2) .LT. ENDT) GO TO 320
    GO TO 370
C
C   TEST SYSTEM CLOCK FOR IMMINENT TIMER OVERFLOW.
C
320 CALL TCK
    CALL TSET(4,KOOCFX)
    GO TO 325,325,KOOCFX
325 BIG=4A TREG(4),TREG(5),TREG(6),TREG(7),TREG(8))
    DO 330 J=1,5
    IF(BIG .EQ. TREG(J+3)) GO TO 335
330 CONTINUE
335 IF(J-LAM) 340,345,340
340 KEY(LAM)=1
    JACK=1
345 LAM=J
    KEY(LAM)=4
    GO TO 135
C
C   ERROR COMMENT OUTPUTS.
C
350 WRITE(6,430) TREG(2)
    GO TO 365
355 WRITE(6,435) TREG(2)

```

```

RATE1180
RATE1185
RATE1190
RATE1195
RATE1200
RATE1205
RATE1210
RATE1215
RATE1220
RATE1225
RATE1230
RATE1235
RATE1240
RATE1245
RATE1250
RATE1255
RATE1260
RATE1265
RATE1270
RATE1275
RATE1280
RATE1285
RATE1290
RATE1295
RATE1300
RATE1305
RATE1310
RATE1315
RATE1320
RATE1325
RATE1330
RATE1335
RATE1340
RATE1345
RATE1350
RATE1355
RATE1360
RATE1365
RATE1370
RATE1375
RATE1380
RATE1385
RATE1390
RATE1395
RATE1400
RATE1405
RATE1410
RATE1415
RATE1420
RATE1425
RATE1430
RATE1435
RATE1440
RATE1445
RATE1450
RATE1455
RATE1460
RATE1465
RATE1470

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```

GO TO 365
360 WRITE(6,425)
    K=NUMB+3
    WRITE(6,440) (TREG(J),J=2,K),TOTAL
365 IF(KB4 .EQ. 1) GO TO 370
    KB6=2
C
C   TRANSFER ALL RESULTS TO OUTPUT TAPE HERE.
C
370 REWIND 1
    END FILE 3
    IF(IIPLOT .NE. 1) GO TO 380
    END FILE 0
    REWIND 8
    DO 375 K=1,ITEM
    READ(8)SIGH(1),IQ(1),(SIGH(J),IQ(J),J=10,17)
    WRITE(10,520)SIGH(1),IQ(1),(SIGH(J),IQ(J),J=10,17)
375 CONTINUE
    END FILE 0
    REWIND 8
    ITEM=0
380 KNT=0
    WRITE(6,475)
    DO 385 K=1,MOUNT
    READ(1) TREG(2),(TREG(J),J=13,18),DO2,DN2,(KEY(J),J=1,15)
    WRITE(6,510) TREG(2),(TREG(J),J=13,18),DO2,DN2,(KEY(J),J=1,15)
    KNT=KNT+1
    IF(KNT .LT. 50) GO TO 385
    WRITE(6,475)
    KNT=0
385 CONTINUE
    REWIND 1
    GO TO (5,390),KB6
390 REWIND 3
    CALL EXIT
C
395 FORMAT (1P6E12.5)
400 FORMAT(76H1SOLUTION OF THE REACTION RATE EQUATIONS WITH 15 SPECIES
    1 AND 168 REACTIONS. )
405 FORMAT(11H1ALTITUDE =1PE11.4,4H CM.,16H TOTAL DENSITY =1PE12.5,14H
    1 TEMPERATURE =OPF7.2)
410 FORMAT(122H1 TIME(SEC)  N(O-)/CC  N(O+)/CC  N(O2-)/CC  N(O3-)/CC
    1 N(NO2-)/CC  N(O+)/CC  N(O2+)/CC  N(N2+)/CC  N(NO+)/CC  PRODUCTIO
    2N)
415 FORMAT(7I2)
420 FORMAT(14)
425 FORMAT(65H0THE PROGRAM IN TRYING TO GENERATE THE LOG OF A NEGATIVE
    1 NUMBER. )
430 FORMAT(45H0THE INTERGRATING MESH IS VANISHING IN INT AT 1PE11.5,6H
    1 SEC. )
435 FORMAT(47H0THE INTERGRAYING MESH IS VANISHING IN ALGA AT 1PE11.5,6H
    1H SEC. )
440 FORMAT(1P10E10.2)
445 FORMAT(12A6)
450 FORMAT(1H0,12A6)
455 FORMAT(1H0,(6(2X4H A(I,13,2H)=1PE10.3)))
460 FORMAT(1H0,(4(2X4H A(I,13,2H)=1PE10.3)))
465 FORMAT(1H ,(4(2X4HCON(I,13,2H)=1PE10.3)))
470 FORMAT(43H THE INCREMENT IS CONSTANT AT 1.0E-06 SEC. )

```

```

RATE1475
RATE1480
RATE1485
RATE1490
RATE1495
RATE1500
RATE1505
RATE1510
RATE1515
RATE1520
RATE1525
RATE1530
RATE1535
RATE1540
RATE1545
RATE1550
RATE1555
RATE1560
RATE1565
RATE1570
RATE1575
RATE1580
RATE1585
RATE1590
RATE1595
RATE1600
RATE1605
RATE1610
RATE1615
RATE1620
RATE1625
RATE1630
RATE1635
RATE1640
RATE1645
RATE1650
RATE1655
RATE1660
RATE1665
RATE1670
RATE1675
RATE1680
RATE1685
RATE1690
RATE1695
RATE1700
RATE1705
RATE1710
RATE1715
RATE1720
RATE1725
RATE1730
RATE1735
RATE1740
RATE1745
RATE1750
RATE1755
RATE1760
RATE1765

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475 FORMAT(12I1 TIME(SEC)  N(NO)/CC  N(N)/CC  N(NO2)/CC  N(O3)/CC RATE1770
1  N(N2O)/CC  N(O)/CC  N(O2)/CC  N(N2)/CC  KEYS 1 THRU 15 RATE1775
2)  RATE1780
480 FORMAT(22HOREACTION COEFFICIENTS)  RATE1785
485 FORMAT(1H ,(6(2X4HCON(,13,2H)=1PE10.3)))  RATE1790
490 FORMAT(1H0,20X,86H THE FOLLOWING IS A LIST OF RATE CONSTANT CHANGES RATE1795
1 FROM THE STD LIST USED IN THIS RUN. )  RATE1800
495 FORMAT(102H1 TIME (SEC) O2 DENSITY N2 DENSITY  E O= O2- ORATE1805
12= NO2- O+ O2+ N2+ NO N NO2 O3 NO+ N2O O )  RATE1810
500 FORMAT(14,1PE10.2,0PF5.1,1PE10.2,7A6)  RATE1815
505 FORMAT(1P11E11.3)  RATE1820
510 FORMAT(1P9E11.3,5I2,1X,4I2,1X,6I2)  RATE1825
515 FORMAT(1H1)  RATE1830
520 FORMAT(6X11,A1,15)  RATE1835
END  RATE1840

```

$$\begin{aligned}
N_{j4} &= N_{j0} + \frac{1}{2} \Delta t F_j(t_0, N_{10}, N_{20}, N_{30} \dots N_{m0}) \\
&\quad - \frac{3}{2} \Delta t F_j(t_0 + \frac{1}{3} \Delta t, N_{12}, N_{22}, N_{32} \dots N_{m2}) \\
&\quad + 2 \Delta t F_j(t_0 + \frac{1}{2} \Delta t, N_{13}, N_{23}, N_{33} \dots N_{m3}) \\
N_{j5} &= N_{j0} + \frac{1}{5} \Delta t F_j(t_0, N_{10}, N_{20}, N_{30} \dots N_{m0}) \\
&\quad + \frac{2}{3} \Delta t F_j(t_0 + \frac{1}{2} \Delta t, N_{13}, N_{23}, N_{33} \dots N_{m3}) \\
&\quad + \frac{1}{6} \Delta t F_j(t + \Delta t, N_{14}, N_{24}, N_{34} \dots N_{m4}) .
\end{aligned}$$

Merson (1957) has shown that the error in  $N_{j4}$  is  $-\frac{1}{120} \Delta t^5 N_j^{(V)}$  and that the error in  $N_{j5}$  is  $-\frac{1}{720} \Delta t^5 N_j^{(V)}$ . Therefore, a good estimate of the error in  $N_{j5}$  which are the accepted values of  $N_j$  at the end of the increment is

$$\frac{1}{5} (N_{j4} - N_{j5}) .$$

The criterion for the acceptance of a solution is that one-fifth of the relative difference between  $N_{j4}$  and  $N_{j5}$  must be less than  $\epsilon$  for every  $N_j$ . That is

$$\frac{|N_{j4} - N_{j5}|}{5 N_{j5}} < \epsilon .$$

Should this criterion fail for any  $N_j$ , the program cuts the increment in half, re-initializes itself, and computes a solution over a smaller increment. It uses this

factor of two cutback for the first three failures. If the solution is still unable to satisfy the criterion after these three tries, the increment is cut by a factor of ten and a new solution is computed. The program then tries to obtain an acceptable solution three times using decade cutbacks. Should the solution still be unacceptable after these three attempts, all the differential equations are returned to the set, the increment is cut another decade, and a new solution is computed. Should the solution still be unacceptable, decade cutbacks are continued until an acceptable solution is obtained or until the increment is reduced below  $10^{-8}$ . If no solution is acceptable by the time the increment is reduced to  $10^{-8}$ , the integration is stopped, the JAKE switch is set to two, and control is transferred to the main program.

This program sets two switches that are used externally to determine conditions under which the solution was generated.

- 1) IFAIL - INTEG will return with this switch on zero if the solution was generated over the first increment used. If the subprogram had to reduce the increment, this switch is set to one. This information is required if the main program is looking for solutions at specific times.
- 2) JAKE - this switch is set to its normal setting of one by the main program. As long as a valid solution is generated, its setting remains on one. If the integrator is unable for any reason to develop a solution with any increment greater than  $10^{-8}$ , this switch is set to two and control is transferred to the main program where the comment THE INTEGRATING MESH IS VANISHING IN INT AT X.XX SEC is written.

This subprogram calls ALGA for a solution to the exponential equations after the computation of each of the five sets of  $N_j$ . In this way, the program always uses a consistent set of  $N_j$ 's every time a derivative computation is called for.

If ALGA returns to INTEG with the JAM switch on two indicating that ALGA could not solve the exponential set of equations, INTEG makes one of two decisions to remedy the difficulty.

- 1) If the concentration of any species is being computed from its exponential equation over the current increment and was computed from its differential over the preceding increment, its differential equation is returned to the differential set and its exponential equation is removed from the exponential set. The system is reinitialized and the integration is started again over the current increment.

- 2) If condition 1 does not prevail, all of the differential equations are returned to the differential set, the exponential set is emptied, the increment is reduced by a factor of ten, the system is reinitialized, and the integration is performed over the smaller increment.

A COMMON subscripted variable TREG is required by the subroutine. Its dimension is (6\*NUMB+4) where NUMB is the number of differential equations in the full set. After each integration, the locations of TREG contain the following values:

TREG(2) = Independent variable t(sec)  
 TREG(3) = Integrating increment  
 TREG(4) - TREG(NUMB+3) = Dependent variables  $N_{j5}$ .

The increment for the next integration is automatically set to twice the value used for the integration just completed. If the new increment is too large it will be cut back by the program during the next integration.

The following statements, beginning on page 81, are a listing of this subroutine.

### 7.1.3 THE ITERATION SUBROUTINE ALGA

This routine solves the simultaneous set of exponential equations. It is called by subroutine INTEG except when the set of differential equations is empty when it is called by the main program. The set of exponential equations (see Eq. 3) is solved by the method of successive substitutions using  $N_0$  as the initial guess and computing successive guesses from

$$N_{j+1} = \frac{N_j + N_{j-1}}{2} \quad j = 0, 1, 2, 3, \dots \text{ITER} .$$

The solution is said to converge if

$$(1-\delta) \leq \frac{N_{j-1}}{N_j} \leq (1+\delta) \quad (45)$$

where  $\delta$  is some number less than one. Choice of the value of  $\delta$  is determined by the amount of charge imbalance that can be tolerated in the solution. Generally, the problem of charge imbalance can be neglected if  $\delta$  is less than 0.001.

If the criterion (Eq. 45) cannot be satisfied within ITER iterations, ALGA makes one of two decisions.

- 1) If any differential equation is still in the differential set the JAM switch is set to two and control is returned to INTEG (see INTEG for remedy taken).

```

$IBFTC INTEG LIST                                INT00000
SUBROUTINE INTEG                                INT00005
C INTEGRATOR USING THE KUTTA MERSON TECHNIQUE.  INT00010
COMMON TREG(15),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGININT00015
1(15)                                           INT00020
COMMON NUMB,EUBAR,ELBAR,D,DO2,DN2,T,PNE,PNO,PO2,PO,PN2,TOTAL,JACK,INT00025
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOTINT00030
20,TOTN                                          INT00035
DIMENSION C(7)                                  INT00040
DATA C/0.33333333,0.16666666,0.125,0.375,0.5,1.5,0.66666666/ INT00045
N1=NUMB+4                                       INT00050
N2=LINT                                          INT00055
N3=I2NT                                          INT00060
N4=K2NT                                          INT00065
N5=J2NT                                          INT00070
N6=N2NT                                          INT00075
KOUNT=0                                          INT00080
DO 5 J=1,NUMB                                   INT00085
TREG(N2)=TREG(J+3)                              INT00090
5 N2=N2+1                                       INT00095
N2=LINT                                          INT00100
TREG(1)=TREG(2)                                 INT00105
10 DO 90 I=1,5                                  INT00110
CALL DAUX                                        INT00115
DO 50 J=1,NUMB                                   INT00120
IF(KEY(J)-1) 45,15,45                           INT00125
15 GO TO (20,25,30,35,40),I                    INT00130
20 TREG(N3)=TREG(N1)*TREG(3)                   INT00135
TREG(J+3)=TREG(N2)+C(1)*TREG(N3)              INT00140
GO TO 45                                         INT00145
25 TREG(J+3)=TREG(N2)+C(2)*TREG(N3)+C(2)*TREG(3)*TREG(N1) INT00150
GO TO 45                                         INT00155
30 TREG(N4)=TREG(N1)*TREG(3)                   INT00160
TREG(J+3)=TREG(N2)+C(3)*TREG(N3)+C(4)*TREG(N4) INT00165
GO TO 45                                         INT00170
35 TREG(N5)=TREG(N1)*TREG(3)                   INT00175
TREG(J+3)=TREG(N2)+C(5)*TREG(N3)-C(6)*TREG(N4)+2.0*TREG(N5) INT00180
TREG(N6)=TREG(J+3)                              INT00185
GO TO 45                                         INT00190
40 TREG(J+3)=TREG(N2)+C(2)*TREG(N3)+C(7)*TREG(N5)+C(2)*TREG(3)*TREG(N INT00195
11)                                              INT00200
45 N1=N1+1                                       INT00205
N2=N2+1                                       INT00210
N3=N3+1                                       INT00215
N4=N4+1                                       INT00220
N5=N5+1                                       INT00225
N6=N6+1                                       INT00230
50 CONTINUE                                       INT00235
N1=NUMB+4                                       INT00240
N2=LINT                                          INT00245
N3=I2NT                                          INT00250
N4=K2NT                                          INT00255
N5=J2NT                                          INT00260
N6=N2NT                                          INT00265
DO 55 K=1,NUMB                                   INT00270
IF(KEY(K)-2) 55,60,55                           INT00275
55 CONTINUE                                       INT00280
GO TO 70                                         INT00285
60 CALL ALGA.                                    INT00290

```

L=JAKE	INT00295
GO TO (65,65,195),L	INT00300
65 L=JAM	INT00305
GO TO (70,110),L	INT00310
70 GO TO (75,90,80,85,90),I	INT00315
75 TREG(2)=TREG(1)+C(1)*TREG(3)	INT00320
GO TO 90	INT00325
80 TREG(2)=TREG(1)+C(5)*TREG(3)	INT00330
GO TO 90	INT00335
85 TREG(2)=TREG(1)+TREG(3)	INT00340
90 CONTINUE	INT00345
DO 105 J=1,NUMB	INT00350
IF(KEY(J)-1) 100,95,100	INT00355
95 IF((ABS(1.0-(TREG(N6)/TREG(J+3)))/5.0) .GT. EUBAR) GO TO 135	INT00360
100 N6=N6+1	INT00365
105 CONTINUE	INT00370
N6=N2NT	INT00375
GO TO 185	INT00380
110 DO 120 J=1,NUMB	INT00385
IF(KEY(J)-2) 120,115,120	INT00390
115 IF(LKEY(J)-1) 120,125,120	INT00395
120 CONTINUE	INT00400
GO TO 165	INT00405
125 KEY(J)=1	INT00410
DO 130 J=1,NUMB	INT00415
TREG(J+3)=TREG(N2)	INT00420
130 N2=N2+1	INT00425
GO TO 155	INT00430
135 KOUNT=KOUNT+1	INT00435
IF(KOUNT .GT. 3) GO TO 160	INT00440
TREG(3)=TREG(3)/2.0	INT00445
140 DO 145 J=1,NUMB	INT00450
TREG(J+3)=TREG(N2)	INT00455
145 N2=N2+1	INT00460
GO TO (155,150),JACK	INT00465
150 IF(TREG(3) .LT. 1.0E-8) GO TO 190	INT00470
155 TREG(2)=TREG(1)	INT00475
N2=LINT	INT00480
N6=N2NT	INT00485
GO TO 10	INT00490
160 IF(KOUNT .LT. 6) GO TO 180	INT00495
165 DO 175 J=1,NUMB	INT00500
IF(KEY(J)-2) 175,170,175	INT00505
170 KEY(J)=1	INT00510
175 CONTINUE	INT00515
180 TREG(3)=TREG(3)/10.0	INT00520
GO TO 140	INT00525
185 TREG(3)=2.0*TREG(3)	INT00530
GO TO 195	INT00535
190 JAKE=2	INT00540
195 RETURN	INT00545
END	INT00550



- 2). If the differential equation set is empty the integrating mesh is halved, the initial conditions are restored, and the iteration procedure is repeated.

Should ALGA be unable to compute a solution to the full set of exponential equations before the increment is reduced to the starting increment (usually  $10^{-6}$  secs), the JAKE switch is set to three and control is returned to the main program where the comment THE INTEGRATING MESH IS VANISHING IN ALGA AT X, XX SEC is written.

The following statements, beginning on page 84, are a listing of subroutine ALGA.

#### 7.1.4 SUBROUTINE TO COMPUTE THE FORM AND REMV TERMS, SLOP

This subroutine computes the  $\sum F_i$  and  $\sum R_i$  terms required in computing the derivatives. This has always been a tedious program to write because it is here that the sum of all the rates at which the species are formed and removed is computed. For a large number of reactions and species the effort to hand code this program is tremendous.

A program was written by David McIntyre (1965) for an IBM-6000 computer which, upon being fed in coded form the reactions and the species, writes a program for computing the total and the partial derivatives of each species. This code was rewritten by the author for use on an IBM-7044-7094 computer to compute only the formation and the removal equations required for each species. This program in its latest version is described in Appendix B.

Since the  $\sum F_i$  and  $\sum R_i$  terms are required by both INTEG and ALGA, SLOP is written in such a way that it can be called by either of these subroutines. In order to conserve computer time, SLOP is so written that only the FORM(J) and the REMV(J) terms for the species that are not in equilibrium are computed when SLOP is called by INTEG(KIND=1) and only the FORM(J) and the REMV(J) terms for the species that are in equilibrium are computed when SLOP is called by ALGA (KIND=2). This eliminates the waste of time in computing derivatives that will not be used. In addition, SLOP calls PRODUC for the rate of production of ionization by the external source only when SLOP is called by INTEG.

Subroutine SLOP is now written by the computer. The following statements, beginning on page 85, are written for 15 species and 168 reactions.

31BFTC ALGA LIST	ALGA0000
SUBROUTINE ALGA	ALGA0005
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGINALGA0010	ALGA0015
1(15)	ALGA0020
COMMON NUMB,EUBAR,ELBAR,D,DU2,DN2,T,PNE,PND,PO2,PO,PN2,TOTAL,JACK,ALGA0025	ALGA0030
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOTALGA0025	ALGA0035
20,TOTN	ALGA0040
DIMENSION Y(17),RAV(17),ZINCH(17)	ALGA0045
DO 5 J=1,NUMB	ALGA0050
Y(J)=TREG(J+3)	ALGA0055
ZINCH(J)=TREG(J+3)	ALGA0060
RAT(J)=0.0	ALGA0065
5 CONTINUE	ALGA0070
10 KOUNT=0	ALGA0075
15 KIND=2	ALGA0080
CALL SLOP(KIND)	ALGA0085
FORM(10)=FORM(10)-PND	ALGA0090
FORM(15)=FORM(15)-PO	ALGA0095
DO 30 J=1,NUMB	ALGA0100
IF(KEY(J)-2) 30,20,30	ALGA0105
20 YEJK=FORM(J)/REMV(J)	ALGA0110
YIPES=ABS(REMV(J)*TREG(3))	ALGA0115
IF(YIPES.GT. 30.0) GO TO 25	ALGA0120
Y(J)=(ZINCH(J)-YEJK)*EXP(-YIPES)+YEJK	ALGA0125
GO TO 30	ALGA0130
25 Y(J)=YEJK	ALGA0135
30 CONTINUE	ALGA0140
35 DO 45 J=1,NUMB	ALGA0145
IF(KEY(J)-2) 45,40,45	ALGA0150
40 RAT(J)=(TREG(J+3)/Y(J))	ALGA0155
45 CONTINUE	ALGA0160
DO 60 J=1,NUMB	ALGA0165
IF(KEY(J)-2) 60,50,60	ALGA0170
50 IF(RAT(J)-(1.0+ELBAR)) 55,65,65	ALGA0175
55 IF(RAT(J)-(1.0-ELBAR)) 65,60,60	ALGA0180
60 CONTINUE	ALGA0185
GO TO 110	ALGA0190
65 DO 75 J=1,NUMB	ALGA0195
IF(KEY(J)-2) 75,70,75	ALGA0200
70 TREG(J+3)=(TREG(J+3)+Y(J))/2.0	ALGA0205
75 CONTINUE	ALGA0210
KOUNT=KOUNT+1	ALGA0215
IF(KOUNT-ITER) 15,80,80	ALGA0220
80 DO 85 J=1,NUMB	ALGA0225
IF(KEY(J)-1) 85,105,85	ALGA0230
85 CONTINUE	ALGA0235
TREG(3)=TREG(3)/2.0	ALGA0240
TREG(2)=TREG(2)-TREG(3)	ALGA0245
IF(FIRST-TREG(3)) 95,90,90	ALGA0250
90 JAKE=3	ALGA0255
GO TO 125	ALGA0260
95 L=ITER	ALGA0265
DO 100 J=L,NUMB	ALGA0270
TREG(J+3)=TREG(L)	ALGA0275
L=L+1	ALGA0280
100 CONTINUE	ALGA0285
GO TO 10	ALGA0290
105 JAM=2	ALGA0295
GO TO 125	ALGA0300
110 DO 120 J=1,NUMB	ALGA0305
IF(KEY(J)-2) 120,115,120	ALGA0310
115 TREG(J+3)=(TREG(J+3)+Y(J))/2.0	ALGA0315
120 CONTINUE	ALGA0320
JAM=1	ALGA0325
125 RETURN	
END	

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*IBFTC SLOP LIST
SUBROUTINE SLOP(KIND)
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CONI(168),LKEY(15),BEGINSLOP0010
1(15)
COMMON NUMB,EUBAR,ELBAR,D,DD2,DN2,T,PNE,PND,PO2,PO,PN2,TOTAL,JACK,SLOP0020
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOTSLOP0025
20,TOTN
DIMENSION Y(150),C(168)
EQUIVALENCE (Y(1),TREG(4)),(C,CON)
CALL BALAN
Y(16)=DD2
Y(17)=DN2
Y(18)=D
IF(KIND .EQ. 2) GO TO 5
CALL PRODU
5 IF((KIND .EQ. 1 .AND. KEY( 1) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0075
1 1) .NE. 2)) GO TO 10
REMV( 1) =(Y(9)*(+C(32)+C(36)*Y(18)+C(37)*Y(18)+C(41))+Y(15)*(+SLOP0085
1C(16)+C(22)*Y(16)+C(23)*Y(17)+C(26)*Y(16))+Y(7)*(+C(30)+C(34)*Y(18)SLOP0090
1)+C(39))+Y(8)*(+C(31)+C(35)*Y(18)+C(40))+Y(12)*(+C(18)+C(27)*Y(16)SLOP0095
1+C(28)*Y(17))+Y(13)*(+C(19)+C(20)+C(21))+Y(6)*(+C(33)*Y(18)+C(38)SLOP0100
1+C(17)*Y(16)+C(24)*Y(16)*Y(16)+C(25)*Y(16)+Y(17)+C(29)*Y(10)*Y(18)SLOP0105
2)
FORM( 1) =(Y(2)*(+C(2)+C(8)*Y(15)+C(9)*Y(16)+C(10)*Y(11)+C(11)*SLOP0115
1Y(17)+C(12)*Y(10)+C(13)*Y(13))+Y(3)*(Y(15)*(+C(7)+C(15))+C(1)+C(6)SLOP0120
1*Y(17)+C(14)*Y(11)+C(5)*Y(16))+Y(4)*(+C(4)+C(167)*Y(15))+Y(5)*(+C(SLOP0125
13)+C(168)*Y(15)))+PNE
10 IF((KIND .EQ. 1 .AND. KEY( 2) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0135
1 2) .NE. 2)) GO TO 15
REMV( 2) =(Y(6)*(+C(42)+C(58)*Y(11)+C(59)*Y(16)+C(60)*Y(17)+C(6SLOP0145
11)*Y(15))+Y(7)*(+C(46)+C(63)*Y(18))+Y(8)*(+C(50)+C(55)*Y(18))+Y(9)SLOP0150
1*(+C(54)+C(67)*Y(18))+Y(10)*(+C(12)+C(114)*Y(18))+Y(13)*(+C(13)+C(SLOP0155
193))+C(2)+C(8)*Y(15)+C(9)*Y(16)+C(10)*Y(11)+C(11)*Y(17)+C(92)*Y(12)SLOP0160
1)+C(106)*Y(16)+C(124)*Y(16)*Y(16))
FORM( 2) =(Y(1)*Y(15)*(+C(16)+C(22)*Y(16)+C(23)*Y(17))+C(20)*Y(SLOP0170
1(13))+C(94)*Y(3)*Y(15))
15 IF((KIND .EQ. 1 .AND. KEY( 3) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0180
1 3) .NE. 2)) GO TO 20
REMV( 3) =(Y(8)*(+C(51)+C(66)*Y(18)+C(69)+C(70)+C(71)+C(72))+Y(SLOP0190
19)*Y(15))+C(55)+C(68)*Y(18)+C(75)+C(76)+C(77))+Y(15)*(+C(7)+C(15)+C(94)SLOP0195
1)+Y(6)*(+C(43)+C(62)*Y(18))+Y(7)*(+C(47)+C(64)*Y(18))+Y(11)*(+C(14)SLOP0200
1)+C(115)*Y(18))+C(1)+C(5)*Y(16)+C(6)*Y(17)+C(95)*Y(12)+C(96)*Y(13)SLOP0205
1+C(125)*Y(16)*Y(17))
FORM( 3) =(Y(1)*(+C(17)*Y(16)+C(21)*Y(13)+C(24)*Y(16)*Y(16)+C(2SLOP0215
15)*Y(16)*Y(17)+C(26)*Y(16)*Y(15))
20 IF((KIND .EQ. 1 .AND. KEY( 4) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0225
1 4) .NE. 2)) GO TO 25
REMV( 4) =(Y(9)*(+C(57)+C(81)+C(82))+Y(8)*(+C(53)+C(74))+C(4)+CSLOP0235
1(45)*Y(6)+C(49)*Y(7)+C(98)*Y(12)+C(126)*Y(17)+C(167)*Y(15))
FORM( 4) =(Y(13)*(+C(19)*Y(1)+C(93)*Y(2)+C(96)*Y(3)+C(97)*Y(5))SLOP0245
1+Y(2)*(+C(106)*Y(16)+C(126)*Y(16)*Y(16))
25 IF((KIND .EQ. 1 .AND. KEY( 5) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0255
1 5) .NE. 2)) GO TO 30
REMV( 5) =(Y(9)*(+C(56)+C(78)+C(79)+C(80))+Y(8)*(+C(52)+C(73))+SLOP0265
1C(3)+C(44)*Y(6)+C(48)*Y(7)+C(97)*Y(13)+C(168)*Y(15))
FORM( 5) =(Y(12)*Y(1)*(+C(18)+C(27)*Y(16)+C(28)*Y(17))+C(92)*Y(SLOP0275
1(2)+C(95)*Y(3)+C(98)*Y(4))+Y(3)*(+C(115)*Y(11)*Y(18)+C(125)*Y(16)SLOP0280
1Y(17))+C(114)*Y(2)*Y(10)*Y(18)+C(126)*Y(4)*Y(17))
30 IF((KIND .EQ. 1 .AND. KEY( 6) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0290

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1 6) .NE. 2) GO TO 35 SLOP0295
REHV( 6) =(Y(2)*(+C(42)+C(59)*Y(11)+C(59)*Y(16)+C(60)*Y(17)+C(65)SLOP0300
11)*Y(15))+Y(10)*(+C(84)+C(102)+C(110)*Y(18)+C(117))+Y(1)*(+C(33)*YSLOP0305
1(18)+C(38))+Y(3)*(+C(43)+C(62)*Y(18))+Y(11)*(+C(100)+C(108)*Y(18))SLOP0310
1+Y(15)*(+C(99)+C(107)*Y(18)+C(83)*Y(16)+C(85)*Y(12)+C(86)*Y(14)+CSLOP0315
1(101)*Y(17)+C(109)*Y(17)*Y(18)+C(116)*Y(17)+C(44)*Y(5)+C(45)*Y(4))SLOP0320
FORM( 6) =(+C(118)*Y(7)*Y(11)+C(88)*Y(8)*Y(15))+PO SLOP0325
35 IF((KIND .EQ. 1 .AND. KEY( 7) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0330
1 7) .NE. 2)) GO TO 40 SLOP0335
REHV( 7) =(Y(1)*(+C(30)+C(34)*Y(18)+C(39))+Y(2)*(+C(46)+C(63)*YSLOP0340
1(18))+Y(3)*(+C(47)+C(64)*Y(18))+Y(11)*(+C(118)+C(120))+Y(15)*(+C(15)SLOP0345
103)+C(111)*Y(18)+C(87)*Y(10)+C(119)*Y(17)+C(121)*Y(12)+C(48)*Y(5))SLOP0350
1+C(49)*Y(4)) SLOP0355
FORM( 7) =(Y(6)*Y(15)*(+C(99)+C(107)*Y(18))+C(117)*Y(10)+C(83)SLOP0360
1*Y(16))+C(89)*Y(8)*Y(16))+PO2 SLOP0365
40 IF((KIND .EQ. 1 .AND. KEY( 8) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0370
1 8) .NE. 2)) GO TO 45 SLOP0375
REHV( 8) =(Y(3)*(+C(51)+C(66)*Y(18)+C(69)+C(70)+C(71)+C(72))+Y(SLOP0380
11)*(+C(31)+C(35)*Y(18)+C(40))+Y(2)*(+C(50)+C(65)*Y(18))+Y(4)*(+C(55)SLOP0385
13)+C(74))+Y(5)*(+C(52)+C(73))+Y(15)*(+C(88)+C(122))+C(89)*Y(16)+C(SLOP0390
190)*Y(11)+C(91)*Y(10)+C(104)*Y(17)+C(123)*Y(16)) SLOP0395
FORM( 8) =+PN2 SLOP0400
45 IF((KIND .EQ. 1 .AND. KEY( 9) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0405
1 9) .NE. 2)) GO TO 50 SLOP0410
REHV( 9) =(Y(3)*(+C(55)+C(68)*Y(18)+C(75)+C(76)+C(77))+Y(1)*(+CSLOP0415
1(32)+C(36)*Y(18)+C(37)*Y(18)+C(41))+Y(5)*(+C(56)+C(78)+C(79)+C(80))SLOP0420
1)+Y(4)*(+C(57)+C(81)+C(82))+Y(2)*(+C(54)+C(67)*Y(18))+Y(15)*(+C(10)SLOP0425
15)+C(112)*Y(18))+C(113)*Y(11)*Y(18)) SLOP0430
FORM( 9) =(Y(6)*Y(11)*(+C(100)+C(108)*Y(18))+C(116)*Y(17)+C(84)SLOP0435
1)*Y(10))+Y(7)*(+C(119)*Y(17)+C(120)*Y(11)+C(121)*Y(12)+C(87)*Y(10))SLOP0440
1)+Y(8)*(+C(122)*Y(15)+C(123)*Y(16)+C(91)*Y(10))+PNO SLOP0445
50 IF((KIND .EQ. 1 .AND. KEY(10) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0450
110) .NE. 2)) GO TO 55 SLOP0455
REHV(10) =(Y(6)*(+C(84)+C(102)+C(110)*Y(18)+C(117))+Y(15)*(+C(15)SLOP0460
131)+C(143)*Y(16)+C(144)*Y(17)+C(150))+Y(11)*(+C(134)+C(147)*Y(18)+SLOP0465
1C(156))+Y(2)*(+C(12)+C(114)*Y(18))+Y(10)*(+C(148)*Y(16)+C(148)*Y(15)SLOP0470
16))+C(20)*Y(11)*Y(18)+C(160)*Y(13)+C(162)+C(87)*Y(7)+C(91)*Y(8)) SLOP0475
FORM(10) =(Y(9)*Y(1)*(+C(36)*Y(18)+C(41))+Y(3)*(+C(55)+C(68)*YSLOP0480
1(18))+Y(5)*(+C(79)+C(56))+C(54)*Y(2)+C(57)*Y(4))+Y(11)*Y(12)*(+C(SLOP0485
1158)+C(158))+Y(15)*(+C(129)+C(141)*Y(18))+C(10)*Y(2)+C(155)*Y(16)+SLOP0490
1C(118)*Y(7))+Y(15)*(Y(14)*(+C(152)+C(152))+C(149)*Y(17)+C(151)*Y(15)SLOP0495
12)+C(168)*Y(5))+Y(8)*Y(3)*(+C(69)+C(69))+C(73)*Y(5)+C(123)*Y(16))SLOP0500
1+C(163)*Y(12)+C(119)*Y(7)*Y(17)+C(126)*Y(4)*Y(17)+C(165)*Y(14)) SLOP0505
55 IF((KIND .EQ. 1 .AND. KEY(11) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0510
111) .NE. 2)) GO TO 60 SLOP0515
REHV(11) =(Y(11)*(+C(132)+C(145)*Y(18)+C(132)+C(145)*Y(18))+Y(6)SLOP0520
1)*(+C(100)+C(108)*Y(18)+C(58)*Y(2))+Y(10)*(+C(134)+C(147)*Y(18)+C(SLOP0525
1156))+Y(12)*(+C(157)+C(158)+C(159))+Y(3)*(+C(14)+C(115)*Y(18))+Y(7)SLOP0530
1)*(+C(118)+C(127))+Y(15)*(+C(129)+C(141)*Y(18))+C(133)*Y(16)+C(146)SLOP0535
1)*Y(16)*Y(18)+C(155)*Y(16)+C(10)*Y(2)+C(190)*Y(18)+C(113)*Y(9)*Y(18)SLOP0540
1) SLOP0545
FORM(11) =(Y(9)*Y(1)*(+C(32)+C(37)*Y(18))+Y(3)*(+C(76)+C(77))+SLOP0550
1Y(5)*(+C(78)+C(79))+C(81)*Y(4))+Y(8)*Y(3)*(+C(72)+C(71)+C(72))+Y(SLOP0555
11)*(+C(31)+C(31))+C(122)*Y(15))+Y(6)*(+C(58)*Y(2)*Y(11)+C(116)*Y(15)SLOP0560
17)+C(117)*Y(10))+Y(10)*(+C(162)+C(150)*Y(15))+C(165)*Y(14)+C(149)*SLOP0565
1Y(15)*Y(17)) SLOP0570
60 IF((KIND .EQ. 1 .AND. KEY(12) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0575
112) .NE. 2)) GO TO 65 SLOP0580
REHV(12) =(Y(1)*(+C(18)+C(27)*Y(16)+C(28)*Y(17))+Y(11)*(+C(157)SLOP0585

```

```

1+C(158)+C(159))+C(163)+C(85)*Y(6)+C(92)*Y(2)+C(95)*Y(3)+C(98)*Y(4)SLOP0590
1+C(121)*Y(7)+C(151)*Y(15)) SLOP0595
FORM(12) =(Y(10)*Y(15)*C(131)+C(143)*Y(16)+C(144)*Y(17))+Y(1)SLOP0600
10)*C(148)*Y(16)+C(148)*Y(16))+C(12)*Y(2)+C(160)*Y(13))+Y(5)*C(5)SLOP0605
13)+C(44)*Y(6)+C(48)*Y(7)+C(56)*Y(9)+C(97)*Y(13)+C(52)*Y(8))+Y(3)*(SLOP0610
1+C(14)*Y(11)+C(71)*Y(8)+C(75)*Y(9)+C(125)*Y(16)*Y(17))+Y(9)*C(67)SLOP0615
1)*Y(2)*Y(18)+C(82)*Y(4))+Y(11)*C(133)*Y(16)+C(146)*Y(16)*Y(18))SLOP0620
65 IF((KIND .EQ. 1 .AND. KEY(13) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0625
113) .NE. 2)) GO TO 70 SLOP0630
REMV(13) =(Y(1)*C(19)+C(20)+C(21))+Y(2)*C(13)+C(93))+C(166)SLOP0635
1+C(96)*Y(3)+C(97)*Y(5)+C(154)*Y(15)+C(160)*Y(10)) SLOP0640
FORM(13) =(Y(4)*C(4)+C(45)*Y(6)+C(49)*Y(7)+C(57)*Y(9)+C(98)*Y(SLOP0645
112)+C(53)*Y(8))+Y(15)*C(15)*Y(3)+C(128)*Y(16)+C(138)*Y(16)*Y(16)SLOP0650
1)+C(139)*Y(16)*Y(17)+C(140)*Y(16)*Y(15))+Y(2)*C(9)*Y(16)+C(63)*Y(SLOP0655
17)*Y(18))+Y(3)*C(62)*Y(6)*Y(18)+C(76)*Y(9))+C(80)*Y(5)*Y( )+C(1)SLOP0660
121)*Y(7)*Y(12)) SLOP0665
70 IF((KIND .EQ. 1 .AND. KEY(14) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0670
114) .NE. 2)) GO TO 75 SLOP0675
REMV(14) =(Y(15)*C(152)+C(153))+C(164)+C(165)+C(86)*Y(6)) SLOP0680
FORM(14) =(Y(8)*C(65)*Y(2)*Y(16)+C(70)*Y(3)+C(73)*Y(5)+C(74)*SLOP0685
1Y(4))+Y(11)*Y(10)*C(134)+C(147)*Y(18))+C(159)*Y(12))+Y(15)*C(SLOP0690
1130)*Y(17)+C(142)*Y(17)*Y(18))+C(11)*Y(2)*Y(17)) SLOP0695
75 IF((KIND .EQ. 1 .AND. KEY(15) .NE. 1) .OR. (KIND .EQ. 2 .AND. KEY(SLOP0700
115) .NE. 2)) GO TO 80 SLOP0705
REMV(15) =(Y(15)*Y(15)*C(136)+C(136)+C(136))+C(127)+C(135)*Y(SLOP0710
1116)+C(137)*Y(17)+C(140)*Y(16)+C(127)+C(135)*Y(16)+C(137)*Y(17)+C(SLOP0715
1140)*Y(16))+Y(1)*C(16)+C(22)*Y(16)+C(23)*Y(17)+C(26)*Y(16))+Y(10)SLOP0720
1)*C(131)+C(143)*Y(16)+C(144)*Y(17)+C(150))+Y(3)*C(7)+C(15)+C(9)SLOP0725
14))+Y(6)*C(99)+C(107)*Y(18)+C(61)*Y(2))+Y(7)*C(103)+C(111)*Y(1)SLOP0730
181))+Y(8)*C(88)+C(122))+Y(9)*C(105)+C(112)*Y(18))+Y(11)*C(129)SLOP0735
1)+C(141)*Y(18))+Y(14)*C(152)+C(153)+C(128)*Y(16)+C(130)*Y(17)+C(SLOP0740
11138)*Y(16)*Y(16)+C(139)*Y(16)*Y(17)+C(142)*Y(17)*Y(18)+C(149)*Y(1)SLOP0745
171)+C(151)*Y(12)+C(154)*Y(13)+C(8)*Y(2)+C(167)*Y(4)+C(168)*Y(5)) SLOP0750
FORM(15) =(Y(6)*Y(2)*C(42)+C(42)+C(61)*Y(15))+Y(1)*C(33)*Y(SLOP0755
1118)+C(38))+C(83)*Y(16)+C(84)*Y(10)+C(85)*Y(12)+C(86)*Y(14)+C(43)*SLOP0760
1Y(3)+C(44)*Y(5)+C(45)*Y(4))+Y(1)*Y(7)*C(30)+C(30))+Y(9)*C(32)SLOP0765
1+C(37)*Y(38))+C(21)*Y(13)+C(26)*Y(16)*Y(15))+Y(2)*C(2)+C(46)*Y(7)SLOP0770
1)+C(50)*Y(8)+C(54)*Y(9)+C(93)*Y(13)+C(92)*Y(12))+Y(3)*Y(8)*C(70)SLOP0775
1)+C(72))+Y(9)*C(75)+C(77))+C(7)*Y(15))+Y(11)*C(120)*Y(7)+C(155)SLOP0780
1)*Y(16)+C(156)*Y(10)+C(159)*Y(12))+Y(15)*Y(15)+C(136)*Y(15)+C(1)SLOP0785
140)*Y(16))+C(161)*Y(16)+C(166)*Y(13)+C(161)*Y(16)+C(162)*Y(10)+C(SLOP0790
1163)*Y(12)+C(164)*Y(14)) SLOP0795
80 RETURN SLOP0800
END SLOP0805

```

### 7.1.5 SUBROUTINE TO COMPUTE THE DERIVATIVES, DAUX

This subroutine is called by INTEG and computes the derivatives

$$\frac{dN_i}{dt} = \sum F_i - N_j \sum R_i$$

This is a relatively short subroutine since the bulk of the computations are performed in SLOP which computes  $\sum F_i$  and  $\sum R_i$ . If any species is in equilibrium this subroutine sets its derivative to zero. The following statements, beginning on page 88, are a listing for this subroutine.

```

IBFTC DAUX LIST DAUX0000
SUBROUTINE DAUX DAUX0005
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGIN DAUX0010
1(15) DAUX0015
COMMON NUMB,EUBAR,ELBAR,D,DO2,DN2,T,PNE,PNU,PO2,PO,PN2,TOTAL,JACK, DAUX0020
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,K83,TOTO DAUX0025
20,TOTN DAUX0030
KIND=1 DAUX0035
CALL SLOP(KIND) DAUX0040
5 L=NUMB+4 DAUX0045
DO 20 J=1,NUMB DAUX0050
IF(KEY(J) .NE. 1) GO TO 10 DAUX0055
TREG(L)=FORM(J)-(REMV(J)*TREG(J+3)) DAUX0060
GO TO 15 DAUX0065
10 TREG(L)=0.0 DAUX0070
15 L=L+1 DAUX0075
20 CONTINUE DAUX0080
IF(KEY(10) .NE. 1) GO TO 25 DAUX0085
TREG(NUMB+13)=TREG(NUMB+13)-PNU DAUX0090
25 IF(KEY(15) .NE. 1) GO TO 30 DAUX0095
TREG(NUMB+18)=TREG(NUMB+18)-PO DAUX0100
30 RETURN DAUX0105
END DAUX0110

```

#### 7.1.6 SUBROUTINE TO SET INITIAL CONDITIONS, INITAL

This subroutine is incorporated into the package for the purpose of establishing the initial conditions on the solution of the differential equations. In most applications, this is a very simple subroutine. It simply sets the starting time to zero, the initial increment to  $10^{-6}$ , and transfers the initial concentrations read into the BEGIN region to the proper TREG locations. It also computes the total numbers of oxygen (TOTO) and nitrogen (TOTN) atoms initially put into the system.

Since the situation could arise where it would be necessary to use a complicated function to compute the initial concentrations, as in the case of nuclear weapons effects, a separate subprogram is used to permit flexibility in setting up the initial conditions for the solutions without disrupting the entire code. The following locations of TREG must be set by this subroutine.

TREG(2) = 0.0, the starting time in seconds .  
TREG(3) =  $10^{-6}$ , the initial increment in seconds .  
TREG(4) to TREG(NUMB+3) = the initial concentrations of the  
dependent variables  $N_{oi}$ .

The initial increment is always taken as  $10^{-6}$  secs. There could be cases where a species has decayed or build up from its initial value to its equilibrium value in less than  $10^{-6}$  secs. In the event that this should happen the initial integrating increment must be some value smaller than the equilibrium time. If a mesh of  $10^{-6}$  secs is too large, the criterion set on the integration cannot be satisfied and the program will automatically cut it back until it arrives at an increment that can be accepted. If it is known that a species will reach its

equilibrium value before  $10^{-6}$  secs, the increment can be initially set to some smaller value, thus saving computer time.

The following statements are a listing for this code.

```

$18FTC INITIAL LIST                                INIT0000
SUBROUTINE INITIAL                                INIT0005
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGIN(15),
1(15)                                             INIT0010
COMMON NUMB,EUBAR,ELBAR,D,DO2,DN2,T,PNE,PNO,PO2,PO,PN2,TOTAL,JACK,INIT0020
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOTINIT0025
20,TOTN.                                         INIT0030
TREG(2)=0.0                                       INIT0035
TREG(3)=1.0E-6                                    INIT0040
FIRST=TREG(3)                                     INIT0045
DO 5 J=1,15                                       INIT0050
5 TREG(J+3)=BEGIN(J)                             INIT0055
TOTAL=PROD                                        INIT0060
TOTO=TREG(5)+2.0*TREG(6)+3.0*TREG(7)+2.0*TREG(8)+TREG(9)+2.0*TREG(10)+
110)+TREG(12)+2.0*TREG(15)+3.0*TREG(16)+TREG(17)+TREG(13)+TREG(18)+
22.0*002                                          INIT0065
TOTN=TREG(8)+2.0*TREG(11)+TREG(12)+TREG(13)+TREG(14)+TREG(15)+2.0*
1TREG(17)+2.0*DN2                                INIT0070
RETURN                                           INIT0075
END                                               INIT0080

```

#### 7.1.7 SUBROUTINE TO COMPUTE THE EXTERNAL IONIZATION SOURCE FUNCTION, PRODUC

The insertion of any particular ionization source function into the system is facilitated by incorporating a separate subroutine for this purpose. The routine used with the deionization code simply injects a constant rate of production of ion-pairs/cm<sup>3</sup>/sec into the differential equations. For simplicity this constant is read into the computer on one of the input data cards. This production represents the number of electrons produced by some external source other than the chemical equations. For simple deionization problems this constant production rate is partitioned among the positive ions as if it were an ultraviolet source. That is,

$$q(N_2^+) = 0.13926*PROD$$

$$q(O_2^+) = 0.79272*PROD$$

$$q(O^+) = 0.06802*PROD$$

Although the code will handle any time-dependent function it will not operate properly if a sharp discontinuity is encountered in the production function inside of the increment  $\Delta t$ . If discontinuities are present in the source function they must be accommodated for by the main program before the integration is attempted over the time increment in which they exist.





### 7.1.9 SUBROUTINE TO COMPUTE THE HISTORY OF THE REACTIONS, DAUXT

Since it is not possible to determine the actual kinetics of the atmospheric constituents simply by studying the solutions to the differential equations, this program is incorporated to give a snapshot of the chemical reactions whenever it is called.

Each time DAUXT is called, each individual reaction is computed and the entire array of reactions along with the corresponding rate constants and the reaction rates are written on FORTRAN-tape 3. The reactions are written in a pseudochemical notation that is easy to read. By examination of this output it is a simple matter to determine which reactions are responsible for the behavior of any species at any particular time.

Computation of this information is optional. If switch KB2 is on zero the snapshot is taken. If switch KB2 is on one computation of this information is bypassed. There is also an option to print this history after every integration or only once at the beginning of each decade of time. If switch KB3 is on one the history is printed once for each decade of time. If switch KB3 is on zero the history is printed after every integration. These switches are set by one of the input data cards.

The following statements, beginning on page 92, are a listing of this code.

## 7.2 Diurnal Variation Code

The code, as described in Section 7.1, is readily applicable to the problem of the diurnal variation of the atmospheric constituents. The only programs that require any modification are the main program and subroutines PRODUC and BALAN. One additional subprogram is necessary for the computation of the percent obscuration of the visible light from the sun by the solid earth during periods of sunrise and sunset.

### 7.2.1 MAIN PROGRAM DIURN

In addition to the functions described in Section 7.1.1, the main program must also compute the times of sunrise and sunset for the particular altitude and geographic location under consideration. Besides accumulating the time in seconds, the main program must also compute the local solar time in hours. Although the code must start with time equal to zero seconds, this zero time may refer to any local solar time. To accommodate these additional features more input parameters are required. The following are the changes in the input data as described in Section 7.1.1.3.

```

$IBFTC DAUXT LIST                                DXT00000
SUBROUTINE DAUXT                                DXT00005
C                                                DXT00010
C REACTIONS FOR 15 SPECIES.                      DXT00015
COMMON TREG(150),KEY(15),FORM(15),REMV(15),CON(168),LKEY(15),BEGINOX DXT00020
1(15)                                           DXT00025
COMMON NUMB,EUBAR,ELBAR,D,DO2,DN2,T,PNE,PNO,PO2,PO,PN2,TOTAL,JACK, DXT00030
1JAKE,JAM,ITER,LINT,I2NT,K2NT,J2NT,N2NT,FIRST,PROD,LAM,TIME,KB3,TOT DXT00035
20,TOTN                                         DXT00040
DIMENSION R(168)                               DXT00045
C                                                DXT00050
IF(KB3.NE.1) GO TO 5                            DXT00055
IF(TIME.GT. TREG(2)) GO TO 10                 DXT00060
5 DO=TREG(18)                                   DXT00065
R(1)=TREG(6)*CON(1)                            DXT00070
R(2)=TREG(5)*CON(2)                            DXT00075
R(3)=TREG(8)*CON(3)                            DXT00080
R(4)=TREG(7)*CON(4)                            DXT00085
R(5)=TREG(6)*DO2*CON(5)                       DXT00090
R(6)=TREG(6)*DN2*CON(6)                       DXT00095
R(7)=TREG(6)*DO*CON(7)                       DXT00100
R(8)=TREG(5)*DO*CON(8)                       DXT00105
R(9)=TREG(5)*DO2*CON(9)                      DXT00110
R(10)=TREG(5)*TREG(11)*CON(10)                DXT00115
R(11)=TREG(5)*DN2*CON(11)                    DXT00120
R(12)=TREG(5)*TREG(13)*CON(12)               DXT00125
R(13)=TREG(5)*TREG(16)*CON(13)               DXT00130
R(14)=TREG(6)*TREG(14)*CON(14)               DXT00135
R(15)=TREG(6)*DO*CON(15)                     DXT00140
R(16)=TREG(4)*DO*CON(16)                     DXT00145
R(17)=TREG(4)*DO2*CON(17)                    DXT00150
R(18)=TREG(4)*TREG(15)*CON(18)                DXT00155
R(19)=TREG(4)*TREG(16)*CON(19)                DXT00160
R(20)=TREG(4)*TREG(16)*CON(20)                DXT00165
R(21)=TREG(4)*TREG(15)*CON(21)                DXT00170
R(22)=TREG(4)*DO*(DO2*CON(22))               DXT00175
R(23)=TREG(4)*DO*(DN2*CON(23))               DXT00180
R(24)=TREG(4)*DO2*(DO2*CON(24))              DXT00185
R(25)=TREG(4)*DO2*(DN2*CON(25))              DXT00190
R(26)=TREG(4)*DO*(DO2*CON(26))               DXT00195
R(27)=TREG(4)*TREG(15)*(DO2*CON(27))          DXT00200
R(28)=TREG(4)*TREG(15)*(DN2*CON(28))          DXT00205
R(29)=TREG(4)*TREG(13)*(DO*CON(29))           DXT00210
R(30)=TREG(4)*TREG(10)*CON(30)                DXT00215
R(31)=TREG(4)*TREG(11)*CON(31)                DXT00220
R(32)=TREG(4)*TREG(12)*CON(32)                DXT00225
R(33)=TREG(4)*TREG(9)*(DO*CON(33))            DXT00230
R(34)=TREG(4)*TREG(10)*(DO*CON(34))           DXT00235
R(35)=TREG(4)*TREG(11)*(DO*CON(35))           DXT00240
R(36)=TREG(4)*TREG(12)*(DO*CON(36))           DXT00245
R(37)=TREG(4)*TREG(12)*(DO*CON(37))           DXT00250
R(38)=TREG(4)*TREG(9)*CON(38)                 DXT00255
R(39)=TREG(4)*TREG(10)*CON(39)                DXT00260
R(40)=TREG(4)*TREG(11)*CON(40)                DXT00265
R(41)=TREG(4)*TREG(12)*CON(41)                DXT00270
R(42)=TREG(5)*TREG(9)*CON(42)                 DXT00275
R(43)=TREG(6)*TREG(9)*CON(43)                 DXT00280
R(44)=TREG(8)*TREG(9)*CON(44)                 DXT00285
R(45)=TREG(7)*TREG(9)*CON(45)                 DXT00290

```

R( 46)=TREG(5)*TREG(10)*CON(46)	DXT00295
R( 47)=TREG(6)*TREG(10)*CON(47)	DXT00300
R( 48)=TREG(8)*TREG(10)*CON(48)	DXT00305
R( 49)=TREG(7)*TREG(10)*CON(49)	DXT00310
R( 50)=TREG(5)*TREG(11)*CON(50)	DXT00315
R( 51)=TREG(6)*TREG(11)*CON(51)	DXT00320
R( 52)=TREG(8)*TREG(11)*CON(52)	DXT00325
R( 53)=TREG(7)*TREG(11)*CON(53)	DXT00330
R( 54)=TREG(5)*TREG(12)*CON(54)	DXT00335
R( 55)=TREG(6)*TREG(12)*CON(55)	DXT00340
R( 56)=TREG(8)*TREG(12)*CON(56)	DXT00345
R( 57)=TREG(7)*TREG(12)*CON(57)	DXT00350
R( 58)=TREG(5)*TREG(9)*(TREG(14)*CON(58))	DXT00355
R( 59)=TREG(5)*TREG(9)*(DO2*CON(59))	DXT00360
R( 60)=TREG(5)*TREG(9)*(DN2*CON(60))	DXT00365
R( 61)=TREG(5)*TREG(9)*(DO*CON(61))	DXT00370
R( 62)=TREG(6)*TREG(9)*(D*CON(62))	DXT00375
R( 63)=TREG(5)*TREG(10)*(D*CON(63))	DXT00380
R( 64)=TREG(6)*TREG(10)*(D*CON(64))	DXT00385
R( 65)=TREG(5)*TREG(11)*(D*CON(65))	DXT00390
R( 66)=TREG(6)*TREG(11)*(D*CON(66))	DXT00395
R( 67)=TREG(5)*TREG(12)*(D*CON(67))	DXT00400
R( 68)=TREG(6)*TREG(12)*(D*CON(68))	DXT00405
R( 69)=TREG(6)*TREG(11)*CON(69)	DXT00410
R( 70)=TREG(6)*TREG(11)*CON(70)	DXT00415
R( 71)=TREG(6)*TREG(11)*CON(71)	DXT00420
R( 72)=TREG(6)*TREG(11)*CON(72)	DXT00425
R( 73)=TREG(8)*TREG(11)*CON(73)	DXT00430
R( 74)=TREG(7)*TREG(11)*CON(74)	DXT00435
R( 75)=TREG(6)*TREG(12)*CON(75)	DXT00440
R( 76)=TREG(6)*TREG(12)*CON(76)	DXT00445
R( 77)=TREG(6)*TREG(12)*CON(77)	DXT00450
R( 78)=TREG(8)*TREG(12)*CON(78)	DXT00455
R( 79)=TREG(8)*TREG(12)*CON(79)	DXT00460
R( 80)=TREG(8)*TREG(12)*CON(80)	DXT00465
R( 81)=TREG(7)*TREG(12)*CON(81)	DXT00470
R( 82)=TREG(7)*TREG(12)*CON(82)	DXT00475
R( 83)=TREG(9)*DO2*CON(83)	DXT00480
R( 84)=TREG(9)*TREG(13)*CON(84)	DXT00485
R( 85)=TREG(9)*TREG(15)*CON(85)	DXT00490
R( 86)=TREG(9)*TREG(17)*CON(86)	DXT00495
R( 87)=TREG(10)*TREG(13)*CON(87)	DXT00500
R( 88)=TREG(11)*DO*CON(88)	DXT00505
R( 89)=TREG(11)*DO2*CON(89)	DXT00510
R( 90)=TREG(11)*TREG(14)*CON(90)	DXT00515
R( 91)=TREG(11)*TREG(13)*CON(91)	DXT00520
R( 92)=TREG(5)*TREG(15)*CON(92)	DXT00525
R( 93)=TREG(5)*TREG(16)*CON(93)	DXT00530
R( 94)=TREG(6)*DO*CON(94)	DXT00535
R( 95)=TREG(6)*TREG(15)*CON(95)	DXT00540
R( 96)=TREG(6)*TREG(16)*CON(96)	DXT00545
R( 97)=TREG(8)*TREG(16)*CON(97)	DXT00550
R( 98)=TREG(7)*TREG(15)*CON(98)	DXT00555
R( 99)=TREG(9)*DO*CON(99)	DXT00560
R(100)=TREG(9)*TREG(14)*CON(100)	DXT00565
R(101)=TREG(9)*DN2*CON(101)	DXT00570
R(102)=TREG(9)*TREG(13)*CON(102)	DXT00575
R(103)=TREG(10)*DO*CON(103)	DXT00580
R(104)=TREG(11)*DN2*CON(104)	DXT00585

R(105)=TREG(12)*DO*CON(105)	DXT00590
R(106)=TREG(5)*DO2*CON(106)	DXT00595
R(107)=TREG(9)*DO*(D*CON(107))	DXT00600
R(108)=TREG(9)*TREG(14)*(D*CON(108))	DXT00605
R(109)=TREG(9)*DN2*(D*CON(109))	DXT00610
R(110)=TREG(9)*TREG(13)*(D*CON(110))	DXT00615
R(111)=TREG(10)*DO*(D*CON(111))	DXT00620
R(112)=TREG(12)*DO*(D*CON(112))	DXT00625
R(113)=TREG(12)*TREG(14)*(D*CON(113))	DXT00630
R(114)=TREG(5)*TREG(13)*(D*CON(114))	DXT00635
R(115)=TREG(6)*TREG(14)*(D*CON(115))	DXT00640
R(116)=TREG(9)*DN2*CON(116)	DXT00645
R(117)=TREG(9)*TREG(13)*CON(117)	DXT00650
R(118)=TREG(10)*TREG(14)*CON(118)	DXT00655
R(119)=TREG(10)*DN2*CON(119)	DXT00660
R(120)=TREG(10)*TREG(14)*CON(120)	DXT00665
R(121)=TREG(10)*TREG(15)*CON(121)	DXT00670
R(122)=TREG(11)*DO*CON(122)	DXT00675
R(123)=TREG(11)*DO2*CON(123)	DXT00680
R(124)=TREG(5)*DO2*(DO2*CON(124))	DXT00685
R(125)=TREG(6)*DO2*(DN2*CON(125))	DXT00690
R(126)=TREG(7)*DN2*CON(126)	DXT00695
R(127)=DO*(DO*CON(127))	DXT00700
R(128)=DO*(DO2*CON(128))	DXT00705
R(129)=TREG(14)*DO*CON(129)	DXT00710
R(130)=DO*DN2*CON(130)	DXT00715
R(131)=TREG(13)*DO*CON(131)	DXT00720
R(132)=TREG(14)*TREG(14)*CON(132)	DXT00725
R(133)=TREG(14)*DO2*CON(133)	DXT00730
R(134)=TREG(14)*TREG(13)*CON(134)	DXT00735
R(135)=DO*DO*(DO2*CON(135))	DXT00740
R(136)=DO*DO*(DO*CON(136))	DXT00745
R(137)=DO*DO*(DN2*CON(137))	DXT00750
R(138)=DO*DO2*(DO2*CON(138))	DXT00755
R(139)=DO*DO2*(DN2*CON(139))	DXT00760
R(140)=DO*DO2*(DO*CON(140))	DXT00765
R(141)=TREG(14)*DO*(D*CON(141))	DXT00770
R(142)=DO*(DN2*CON(142))*D	DXT00775
R(143)=DO*TREG(13)*(DO2*CON(143))	DXT00780
R(144)=DO*TREG(13)*(DN2*CON(144))	DXT00785
R(145)=TREG(14)*TREG(14)*(D*CON(145))	DXT00790
R(146)=TREG(14)*(DO2*CON(146))*D	DXT00795
R(147)=TREG(14)*TREG(13)*(D*CON(147))	DXT00800
R(148)=TREG(13)*(DO2*CON(148))*TREG(13)	DXT00805
R(149)=(DO*CON(149))*DN2	DXT00810
R(150)=(DO*CON(150))*TREG(13)	DXT00815
R(151)=(DO*CON(151))*TREG(15)	DXT00820
R(152)=(DO*CON(152))*TREG(17)	DXT00825
R(153)=(DO*CON(153))*TREG(17)	DXT00830
R(154)=(DO*CON(154))*TREG(16)	DXT00835
R(155)=TREG(14)*(DO2*CON(155))	DXT00840
R(156)=TREG(14)*TREG(13)*CON(156)	DXT00845
R(157)=TREG(14)*TREG(15)*CON(157)	DXT00850
R(158)=TREG(14)*TREG(15)*CON(158)	DXT00855
R(159)=TREG(14)*TREG(15)*CON(159)	DXT00860
R(160)=TREG(14)*TREG(16)*CON(160)	DXT00865
R(161)=DO2*CON(161)	DXT00870
R(162)=TREG(13)*CON(162)	DXT00875
R(163)=TREG(15)*CCN(163)	DXT00880

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R(164)=TREG(17)*CCN(164)
R(165)=TREG(17)*CCN(165)
R(166)=TREG(16)*CCN(166)
R(167)=TREG(7)*TREG(18)*CON(167)
R(168)=TREG(8)*TREG(18)*CON(168)
WRITE(3,15)
WRITE(3,20)      TREG(2)
WRITE(3,25)
WRITE(3,30)
WRITE(3,35)      (CON(J),R(J),J=1,4)
WRITE(3,40)
WRITE(3,30)
WRITE(3,45)      (CON(J),R(J),J=5,7)
WRITE(3,50)
WRITE(3,30)
WRITE(3,55)      (CON(J),R(J),J=8,15),(CON(J),R(J),J=167,168)
WRITE(3,60)
WRITE(3,30)
WRITE(3,65)      (CON(J),R(J),J=16,19)
WRITE(3,70)
WRITE(3,30)
WRITE(3,75)      (CON(J),R(J),J=20,21)
WRITE(3,80)
WRITE(3,30)
WRITE(3,85)      (CON(J),R(J),J=22,29)
WRITE(3,90)
WRITE(3,30)
WRITE(3,95)      (CON(J),R(J),J=30,32)
WRITE(3,100)
WRITE(3,30)
WRITE(3,105)     (CON(J),R(J),J=33,37)
WRITE(3,110)
WRITE(3,30)
WRITE(3,115)     (CON(J),R(J),J=38,41)
WRITE(3,120)
WRITE(3,30)
WRITE(3,125)     (CON(J),R(J),J=42,53)
WRITE(3,130)     (CON(J),R(J),J=54,57)
WRITE(3,135)
WRITE(3,30)
WRITE(3,140)     (CON(J),R(J),J=58,68)
WRITE(3,145)
WRITE(3,30)
WRITE(3,150)     (CON(J),R(J),J=69,80)
WRITE(3,155)     (CON(J),R(J),J=81,82)
WRITE(3,160)
WRITE(3,30)
WRITE(3,165)     (CON(J),R(J),J=83,91)
WRITE(3,170)
WRITE(3,30)
WRITE(3,175)     (CON(J),R(J),J=92,98)
WRITE(3,180)
WRITE(3,30)
WRITE(3,185)     (CON(J),R(J),J=99,106)
WRITE(3,190)
WRITE(3,30)
WRITE(3,195)     (CON(J),R(J),J=107,115)
WRITE(3,200)
WRITE(3,30)
DXT00885
DXT00890
DXT00895
DXT00900
DXT00905
DXT00910
DXT00915
DXT00920
DXT00925
DXT00930
DXT00935
DXT00940
DXT00945
DXT00950
DXT00955
DXT00960
DXT00965
DXT00970
DXT00975
DXT00980
DXT00985
DXT00990
DXT00995
DXT01000
DXT01005
DXT01010
DXT01015
DXT01020
DXT01025
DXT01030
DXT01035
DXT01040
DXT01045
DXT01050
DXT01055
DXT01060
DXT01065
DXT01070
DXT01075
DXT01080
DXT01085
DXT01090
DXT01095
DXT01100
DXT01105
DXT01110
DXT01115
DXT01120
DXT01125
DXT01130
DXT01135
DXT01140
DXT01145
DXT01150
DXT01155
DXT01160
DXT01165
DXT01170
DXT01175

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WRITE (3,205) (CON(J),R(J),J=116,123) DXT01180
WRITE(3,210) DXT01185
WRITE(3,30) DXT01190
WRITE (3,215) (CON(J),R(J),J=124,126) DXT01195
WRITE(3,220) DXT01200
WRITE(3,30) DXT01205
WRITE (3,225) (CON(J),R(J),J=127,134) DXT01210
WRITE(3,230) DXT01215
WRITE(3,30) DXT01220
WRITE (3,235) (CON(J),R(J),J=135,146) DXT01225
WRITE (3,260) (CON(147),R(147)) DXT01230
WRITE(3,240) DXT01235
WRITE(3,30) DXT01240
WRITE (3,285) (CON(148),R(148)) DXT01245
WRITE (3,245) (CON(J),R(J),J=149,160) DXT01250
WRITE(3,250) DXT01255
WRITE(3,30) DXT01260
WRITE (3,255) (CON(J),R(J),J=161,166) DXT01265
WRITE (3,265) TOTAL DXT01270
WRITE(3,290) DXT01275
WRITE (3,270) PTNO,PNO,PTO2,PO2,PTO,PO,PTN2,PNZ DXT01280
WRITE (3,295) DXT01285
WRITE(3,290) DXT01290
WRITE (3,275) (J,R(J),J=1,165) DXT01295
WRITE(3,280) (J,R(J),J=166,168) DXT01300
TIME=TIME*10.0 DXT01305
10 RETURN DXT01310
15 FORMAT(1H1,47X28H KINETICS OF THE REACTIONS. ) DXT01315
20 FORMAT(1H0,47X7H TIME =1PE12.5,6H SEC. ) DXT01320
25 FORMAT(19HOPHOTO DETACHMENT. ) DXT01325
30 FORMAT(6H0 NO.,15X8HREACTION,17X16HCONSTANT RATE,6X3HNO.,15X8HDXT01330
1REACTION,17X17HCONSTANT RATE ) DXT01335
35 FORMAT(4X12H1. O2- + HV,9X10H= O2 + E,10X1P2E10.2,4X12H2. O- DXT01340
1+ HV,9X10H= O + E,10X1P2E10.2/4X12H3. NO2- + HV,9X10H= NO2 + EDXT01345
2,10X1P2E10.2,4X12H4. O3- + HV,9X10H= O3 + E,10X1P2E10.2) DXT01350
40 FORMAT(25HOCOLLISIONAL DETACHMENT. ) DXT01355
45 FORMAT(4X12H5. O2- + O2,9X18H= O2 + E + O2,2X1P2E10.2,4X12H6DXT01360
1. O2- + N2,9X18H= O2 + E + N2,2X1P2E10.2/4X11H7. O2- + O,10DXT01365
2X17H= O2 + E + O,3X1P2E10.2) DXT01370
50 FORMAT(25H0ASSOCIATIVE DETACHMENT. ) DXT01375
55 FORMAT(4X11H8. O- + O,10X10H= O2 + E,10X1P2E10.2,4X12H9. O- DXT01380
1+ O2,9X10H= O3 + E,10X1P2E10.2/3X12H10. O- + N,10X10H= NO + DXT01385
2E,10X1P2E10.2,3X13H11. O- + N2,9X10H= N2O + E,10X1P2E10.2/3X13HDXT01390
312. O- + NO,9X10H= NO2 + E,10X1P2E10.2,3X13H13. O- + O3,9X20HDXT01395
4= O2 + E + O2 1P2E10.2/3X12H14. O2- + N,10X10H= NO2 + E,10DXT01400
5X1P2E10.2,3X12H15. O2- + O,10X10H= O3 + E,10X1P2E10.2 /3X13H167DXT01405
6. O3- + O,10X17H= O2 + O2 + E,3X1P2E10.2,2X13H168. NO2- + O,10DXT01410
70X17H= O2 + NO + E,3X1P2E10.2) DXT01415
60 FORMAT(23HORADIATIVE ATTACHMENT. ) DXT01420
65 FORMAT(3X12H16. O + E,10X11H= O- + HV,9X1P2E10.2,3X12H17. O2 DXT01425
1 + E,10X11H= O2- + HV,9X1P2E10.2/3X12H18. NO2 + E,10X11H= NO2- DXT01430
2+ HV,9X1P2E10.2,3X12H19. O3 + E,10X11H= O3- + HV,9X1P2E10.2) DXT01435
70 FORMAT(26HODISSOCIATIVE ATTACHMENT. ) DXT01440
75 FORMAT(3X12H20. O3 + E,10X11H= O- + O2,9X1P2E10.2,3X12H21. O3 DXT01445
1 + E,10X10H= O2- + O,10X1P2E10.2) DXT01450
80 FORMAT(24HOTHREE BODY ATTACHMENT. ) DXT01455
85 FORMAT(3X33H22. O + E + O2 = O- + O2,9X1P2E10.2,3X33H23. DXT01460
10 + E + N2 = O- + N2,9X1P2E10.2/3X33H24. O2 + E + O2DXT01465
2 = O2- + O2,9X1P2E10.2,3X33H25. O2 + E + N2 = O2- + N2,9XDXT01470

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31P2E10.2/3X32H26. O2 + E + O = O2- + O, 10X1P2E10.2, 3X33H27 OXT01475  
 4. NO2 + E + O2 = NO2- + O2, 9X1P2E10.2/3X33H28. NO2 + E + OXT01480  
 5N2 = NO2- + N2, 9X1P2E10.2, 3X32H29. NO + E + M = NO- + M, 10X1P2E10.2  
 6OXT01490  
 90 FORMAT(29HODISSOCIATIVE RECOMBINATION. ) OXT01495  
 95 FORMAT(3X12H30. O2+ + E, 10X10H= O + O, 10X1P2E10.2, 3X12H31. N2+ OXT01500  
 1 + E, 10X10H= M + M, 10X1P2E10.2/3X12H32. NO+ + E, 10X10H= N OXT01505  
 2+ O, 10X1P2E10.2) OXT01510  
 100 FORMAT(27HOTHREE BODY RECOMBINATION. ) OXT01515  
 105 FORMAT(3X32H33. O+ + E + M = O + M, 10X1P2E10.2, 3X32H34. OXT01520  
 102+ + E + M = O2 + M, 10X1P2E10.2/3X32H35. N2+ + E + M OXT01525  
 2 = N2 + M, 10X1P2E10.2, 3X32H36. NO+ + E + M = NO + M, 10X1P2E10.2  
 31P2E10.2/3X32H37. NO+ + E + M = N + O + M, 3X1P2E10.2) OXT01530  
 31P2E10.2/3X32H37. NO+ + E + M = N + O + M, 3X1P2E10.2) OXT01535  
 110 FORMAT(26HORADIATIVE RECOMBINATION. ) OXT01540  
 115 FORMAT(3X12H38. O+ + E, 10X11H= O + HV, 9X1P2E10.2, 3X12H39. O2+ OXT01545  
 1 + E, 10X11H= O2 + HV, 9X1P2E10.2/3X12H40. N2+ + E, 10X11H= N2 OXT01550  
 2+ HV, 9X1P2E10.2, 3X12H41. NO+ + E, 10X11H= NO + HV, 9X1P2E10.2) OXT01555  
 120 FORMAT(32HION-ION MUTUAL NEUTRALIZATION. ) OXT01560  
 125 FORMAT(3X13H42. O- + O+, 9X10H= C + O, 10X1P2E10.2, 3X13H43. O2- OXT01565  
 1 + O+, 9X10H= O2 + O, 10X1P2E10.2/3X13H44. NO2- + O+, 9X10H= NO2 OXT01570  
 2+ O, 10X1P2E10.2, 3X13H45. O3- + O+, 9X10H= O3 + O, 10X1P2E10.2/3X13H46. O- OXT01575  
 34H46. O- + O2+, 8X11H= O + O2, 9X1P2E10.2, 3X14H47. O2- + O2+, 8OXT01580  
 4X11H= O2 + O2, 9X1P2E10.2/3X14H48. NO2- + O2+, 8X11H= NO2 + O2, 9OXT01585  
 51P2E10.2, 3X14H49. O3- + O2+, 8X11H= O3 + O2, 9X1P2E10.2/3X14H50. OXT01590  
 60- + N2+, 8X11H= O + N2, 9X1P2E10.2, 3X14H51. O2- + N2+, 8X11H= OXT01595  
 702 + N2, 9X1P2E10.2/3X14H52. NO2- + N2+, 8X11H= NO2 + N2, 9X1P2E10.2 OXT01600  
 8.2, 3X14H53. O3- + N2+, 8X11H= O3 + N2, 9X1P2E10.2) OXT01605  
 130 FORMAT(3X14H54. O- + NO+, 8X11H= O + NO, 9X1P2E10.2, 3X14H55. O2OXT01610  
 1- + NO+, 8X11H= O2 + NO, 9X1P2E10.2/3X14H56. NO2- + NO+, 8X11H= NO OXT01615  
 22 + NO, 9X1P2E10.2, 3X14H57. O3- + NO+, 8X11H= O3 + NO, 9X1P2E10.2 OXT01620  
 3) OXT01625  
 135 FORMAT(35HOTHREE BODY ION-ION RECOMBINATION. ) OXT01630  
 140 FORMAT(3X32H58. O- + O+ + N = O2 + N, 10X1P2E10.2, 3X33H59. OXT01635  
 10- + O+ + O2 = O2 + O2, 9X1P2E10.2/3X33H60. O- + O3 + N2OXT01640  
 2 = O2 + N2, 9X1P2E10.2, 3X32H61. O- + O+ + O = O2 + O, 10X1P2E10.2  
 31P2E10.2/3X32H62. O2- + O+ + M = O3 + M, 10X1P2E10.2, 3X32H63 OXT01650  
 4. O- + O2+ + M = O3 + M, 10X1P2E10.2/3X39H64. O2- + O2+ + OXT01655  
 5M = O2 + O2 + M, 3X1P2E10.2, 3X32H65. O- + N2+ + M = N2O OXT01660  
 6 + M, 10X1P2E10.2/3X39H66. O2- + N2+ + M = O2 + N2 + M, 3X1P2E10.2 OXT01665  
 72E10.2, 3X32H67. O- + NO+ + M = NO2 + M, 10X1P2E10.2/3X39H68. OXT01670  
 802- + NO+ + M = O2 + NO + M, 3X1P2E10.2) OXT01675  
 145 FORMAT(44HION-ION NEUTRALIZATION WITH REARRANGEMENT. ) OXT01680  
 150 FORMAT(3X14H69. O2- + N2+, 8X11H= NO + NO, 9X1P2E10.2, 3X14H70. O2OXT01685  
 1- + N2+, 8X10H= N2O + O, 10X1P2E10.2/3X14H71. O2- + N2+, 8X10H= NO OXT01690  
 22 + N, 10X1P2E10.2, 3X14H72. O2- + N2+, 8X11H= 2N + 2O, 9X1P2E10.2 OXT01695  
 3/3X14H73. NO2- + N2+, 8X11H= N2O + NO, 9X1P2E10.2, 3X14H74. O3- + NO OXT01700  
 42+, 8X11H= N2O + O2, 9X1P2E10.2/3X14H75. O2- + NO+, 8X10H= NO2 + O OXT01705  
 5, 10X1P2E10.2, 3X14H76. O2- + NO+, 8X11H= N + O3, 9X1P2E10.2/3X14H77 OXT01710  
 677. O2- + NO+, 8X11H= N + O2 + O, 3X1P2E10.2, 3X14H78. NO2- + NO OXT01715  
 70+, 8X10H= NO3 + N, 10X1P2E10.2/3X14H79. NO2- + NO+, 8X11H= NO + O OXT01720  
 82 + N, 3X1P2E10.2, 3X14H80. NO2- + NO+, 8X11H= O3 + N2, 9X1P2E10.2 OXT01725  
 9) OXT01730  
 155 FORMAT(3X14H81. O3- + NO+, 8X11H= O2 + O2 + N, 3X1P2E10.2, 3X14H82 OXT01735  
 182. O3- + NO+, 8X11H= O2 + NO2, 8X1P2E10.2) OXT01740  
 160 FORMAT(27HOPositive CHARGE TRANSFER. ) OXT01745  
 165 FORMAT(3X13H83. O+ + O2, 9X12H= O + O2+, 8X1P2E10.2, 3X13H84. O+ OXT01750  
 1 + NO, 9X12H= O + NO+, 8X1P2E10.2/3X14H85. O+ + NO2, 8X13H= O OXT01755  
 2 + NO2+, 7X1P2E10.2, 3X14H86. O+ + N2O, 8X13H= O + N2O+, 7X1P2E10.2 OXT01760  
 310.2/3X13H87. O2+ + NO, 9X12H= O2 + NO+, 8X1P2E10.2, 3X12H88. N2+ OXT01765

4 + O,10X11H= N2 + O,9X1P2E10.2/3X13H89. N2+ + O2,9X12H= N2 +DXT01770  
 5 O2+,8X1P2E10.2,3X12H90. N2+ + O,10X11H= N2 + N,9X1P2E10.2/3X10X1775  
 63H91. N2+ + NO,9X12H= N2 + NO+,8X1P2E10.2) DXT01780  
 170 FORMAT(27HNEGATIVE CHARGE TRANSFER. ) DXT01785  
 175 FORMAT(3X14H92. O- + NO2,8X13H= O + NO2-,7X1P2E10.2,3X13H93. DXT01790  
 10- + O3,9X12H= O + O3-,8X1P2E10.2/3X12H94. O2- + O,10X11H= O DXT01795  
 22 + O-,9X1P2E10.2,3X14H95. O2- + NO2,8X13H= O2 + NO2-,7X1P2E10 DXT01800  
 30.2/3X13H96. O2- + O3,9X12H= O2 + O3-,8X1P2E10.2,3X13H97. NO2- DXT01805  
 4+ O3,9X12H= NO2 + O3-,8X1P2E10.2/3X14H98. O3- + NO2,8X13H= O3 DXT01810  
 5+ NO2-,7X1P2E10.2) DXT01815  
 180 FORMAT(37HION-NEUTRAL ASSOCIATION (TWO-BODY). ) DXT01820  
 185 FORMAT(3X12H99. O+ + O,10X11H= O2+ + HV,9X1P2E10.2,2X13H100. O+DXT01825  
 1 + N,10X11H= NO+ + HV,9X1P2E10.2/2X14H101. O+ + N2,9X11H= N2O DXT01830  
 2+ + HV,9X1P2E10.2,2X14H102. O+ + NO,9X11H= NO2+ + HV,9X1P2E10.2/DXT01835  
 32X13H103. O2+ + O,10X11H= O3+ + HV,9X1P2E10.2,2X14H104. N2+ + NDXT01840  
 42,9X11H= N4+ + HV,9X1P2E10.2/2X13H105. NO+ + O,10X11H= NO2+ + HV DXT01845  
 5,9X1P2E10.2,2X14H106. O- + O2,9X11H= O3- + HV,9X1P2E10.2) DXT01850  
 190 FORMAT(39HION-NEUTRAL ASSOCIATION (THREE-BODY). ) DXT01855  
 195 FORMAT(2X33H107. O+ + O + M = NO+ + M,10X1P2E10.2,2X33H108 DXT01860  
 1. O+ + N + M = NO+ + M,10X1P2E10.2/2X33H109. O+ + N2 +DXT01865  
 2 M = N2O+ + M,10X1P2E10.2,2X33H110. O+ + NO + M = NO2+ + MDXT01870  
 3,10X1P2E10.2/2X33H111. O2+ + O + M = O3+ + M,10X1P2E10.2,2X DXT01875  
 433H112. NO+ + O + M = NO2+ + M,10X1P2E10.2/2X33H113. NO+ + DXT01880  
 5N + M = N2O+ + M,10X1P2E10.2,2X33H114. O- + NO + M = NO DXT01885  
 62- + M,10X1P2E10.2/2X33H115. O2- + N + M = NO2- + M,10X1P2E10 DXT01890  
 70.2) DXT01895  
 200 FORMAT(37HOCHARGED REARRANGEMENT POSITIVE-ION. ) DXT01900  
 205 FORMAT(2X14H116. O+ + N2,9X10H= NO+ + N,10X1P2E10.2,2X14H117. O DXT01905  
 1+ + NO,9X10H= O2+ + N,10X1P2E10.2/2X13H118. O2+ + N,10X11H= O+DXT01910  
 2 + NO,9X1P2E10.2,2X14H119. O2+ + N2,9X11H= NO+ + NO,9X1P2E10.2 DXT01915  
 3/2X13H120. O2+ + N,10X10H= NO+ + O,10X1P2E10.2,2X15H121. O2+ + DXT01920  
 4NO2,8X11H= NO+ + O3,9X1P2E10.2/2X13H122. N2+ + O,10X10H= NO+ + DXT01925  
 5N,10X1P2E10.2,2X14H123. N2+ + O2,9X11H= NO+ + NO,9X1P2E10.2) DXT01930  
 210. FORMAT(37HOCHARGED REARRANGEMENT NEGATIVE-ION. ) DXT01935  
 215 FORMAT(2X34H124. O- + O2 + O2 = O3- + O2,9X1P2E10.2,2X35H125 DXT01940  
 1. O2- + O2 + N2 = NO2- + NO2,8X1P2E10.2/2X14H126. O3- + N2,9X DXT01945  
 2,11H= NO2- + NO,9X1P2E10.2) DXT01950  
 220. FORMAT(30H(TWO-BODY ATOM RECOMBINATION. ) DXT01955  
 225. FORMAT(2X13H127. C + O,10X11H= O2 + HV,9X1P2E10.2,2X14H128. O DXT01960  
 1 + O2,9X11H= O3 + HV,9X1P2E10.2/2X13H129. N + O,10X11H= NO DXT01965  
 2 + HV,9X1P2E10.2,2X14H130. O + N2,9X11H= N2O + HV,9X1P2E10.2 DXT01970  
 3/2X14H131. O + NO,9X11H= NO2 + HV,9X1P2E10.2,2X13H132. N + DXT01975  
 4N,10X11H= N2 + HV,9X1P2E10.2/2X14H133. N + O2,9X11H= NO2 + MDXT01980  
 5V,9X1P2E10.2,2X14H134. N + NO,9X11H= N2O + HV,9X1P2E10.2) DXT01985  
 230. FORMAT(32H(THREE-BODY ATOM RECOMBINATION. ) DXT01990  
 235. FORMAT(2X34H135. C + O + O2 = O2 + O2,9X1P2E10.2,2X33H136 DXT01995  
 1. O + O + O = O2 + O,10X1P2E10.2/2X34H137. O + O +DXT02000  
 2 N2 = O2 + N2,9X1P2E10.2,2X34H138. O + O2 + O2 = O3 + O DXT02005  
 32,9X1P2E10.2/2X34H139. O + O2 + N2 = O3 + N2,9X1P2E10.2,2X DXT02010  
 433H140. O + O2 + O = O3 + O,10X1P2E10.2/2X33H141. N + DXT02015  
 50 + M = NO+ + M,10X1P2E10.2,2X33H142. O + N2 + M = N2 DXT02020  
 60 + M,10X1P2E10.2/2X34H143. O + NO + O2 = NO2 + O2,9X1P2E10 DXT02025  
 70.2,2X34H144. O + NO + N2 = NO2 + N2,9X1P2E10.2/2X33H145. NO DXT02030  
 8 + N + M = N2 + M,10X1P2E10.2,2X33H146. N + O2 + M DXT02035  
 9 = NO2 + M,10X1P2E10.2) DXT02040  
 240. FORMAT(24H(NEUTRAL REARRANGEMENT. ) DXT02045  
 245. FORMAT(2X14H149. C + N2,9X10H= NO + N,10X1P2E10.2,2X14H150. O DXT02050  
 1 + NO,9X10H= O2 + N,10X1P2E10.2/2X15H151. O + NO2,9X11H= NO DXT02055  
 20- + O2,9X1P2E10.2,2X15H152. O + N2O,8X11H= NO + NO,9X1P2E10 DXT02060



```

3.2/2X15H153. O + N20,8X11H= O2 + N2,9X1P2E10.2,2X14H154. O DXT02065
4 + O3,9X11H= O2 + O2,9X1P2E10.2/2X14H155. N + O2,9X10H= NO DXT02070
5+ O,10X1P2E10.2,2X14H156. N + NO,9X10H= N2 + O,10X1P2E10.2/2XOXT02075
615H157. N + NO2,8X11H= N2 + O2,9X1P2E10.2,2X15H158. N + NOOXT02080
72,8X11H= NO + NO,9X1P2E10.2/2X15H159. N + NO2,8X10H= N20 + OOXT02085
8,10X1P2E10.2,2X14H160. NO + O3,9X11H= NO2 + O2,9X1P2E10.2) DXT02090
250 FORMAT(21H1PHOTO DISSOCIATION. ) DXT02095
255 FORMAT(2X14H161. O2 + HV,9X10H= O + O,10X1P2E10.2,2X14H162. NOXT02100
10 + HV,9X10H= N + O,10X1P2E10.2/2X14H163. NO2 + HV,9X10H= NOOXT02105
2 + O,10X1P2E10.2,2X14H164. N20 + HV,9X10H= N2 + O,10X1P2E10.2OXT02110
3/2X14H165. N20 + HV,9X11H= N + NO,9X1P2E10.2,2X14H166. O3 + DXT02115
4HV,9X11H= O + O2,9X1P2E10.2) DXT02120
260 FORMAT(2X33H147. N + NO + M = N20 + M,10X1P2E10.2) DXT02125
265 FORMAT(18HOSOURCE FUNCTION =1P1E12.5,20H ION PAIRS/CC/SEC. ) DXT02130
270 FORMAT(6X9HNO + HV,7X10H= NO+ + E,7X1P2E10.2,8X9H02 + HV,7X10DXT02135
1H= O2+ + E,7X1P2E10.2/6X9H0 + HV,7X10H= O+ + E,7X1P2E10.2,8XOXT02140
29HN2 + HV,7X10H= N2+ + E,7X1P2E10.2 ) DXT02145
275 FORMAT(5(2X2HR(,13,2H)=1PE14.7)) DXT02150
280 FORMAT(3(2X2HR(,13,2H)=1PE14.7)) DXT02155
285 FORMAT(2X35H148. NO + O2 + NO = NO2 + NO2,8X1P2E10.2) DXT02160
290 FORMAT(1H0) DXT02165
295 FORMAT(1H0,41HRATES AT WHICH REACTIONS ARE PROCEEDING. ) DXT02170
END DXT02175

```

#### 7.2.1.1 Input Parameters

CARD 1 No change.

CARD 2 In addition to EUBAR, ELBAR, and DEL there is a parameter B4 which is the maximum allowable percentage change in the production rate per step. Should the change in production over the next integration step attempt to exceed this amount, the main program will reduce the integrating increment until this requirement is satisfied. This control is necessary to prevent any difficulties that the code might experience in performing the integration, especially around sunrise and sunset when the rate of production of ionization is undergoing its most rapid change. The variable ENDT is replaced by the variable ENDHR. This parameter is set to the total number of local hours over which a solution is to be generated. These hours are counted continuously from the midnight preceding the local hour at which the computations are started.

CARD 3 No change.

CARD 4 In addition to ALT, D, DO2, DN2, and T this card contains the following parameters:

- (1) EAR = the earth's radius in centimeters.
- (2) DECL = the solar declination in degrees.
- (3) CLAT = the latitude in degrees.
- (4) B6 = the noontime ionization rate of O<sub>2</sub> by Lyman beta.
- (5) B7 = the noontime ionization rate of NO by Lyman alpha.
- (6) B8 and B9 = the constants for the linear approximation to the photodissociation rate coefficient for O<sub>2</sub>. This approximation is written in the form  $K = B8 + B9 * (\text{solar zenith angle})$ . The linear approximation is determined by solving the integral

$$k(\lambda) = N(O_2) \cdot \int_{\lambda_1}^{\lambda_2} \sigma_d(\lambda) \cdot \phi_0(\lambda) \cdot e^{-\left(\sigma_a \cdot \int_z^{\infty} N(O_2) \cdot ds\right)} d\lambda$$

for various values of  $\lambda$ . The constants are

120 km	B8 = $4.2 \times 10^{-5}$
	B9 = $2.88 \times 10^{-5}$
110 km	B8 = $3.6 \times 10^{-6}$
	B9 = $4.19 \times 10^{-6}$

CARDS 5-7 The last value read on these cards (ATIME) is the local hour in seconds at which the solution is to start.  
ATIME = 0 is midnight.

CARD 8 No change.

The photoionization rate tables, as computed and punched externally by the photoionization program, are read following CARD 8.

#### 7.2.1.2 Output

In the diurnal variation code two additional parameters appear in the output. These are the local solar time in hours and the value of the solar zenith angle at this time. Because of the inclusion of these parameters in the output, another auxilliary output tape is required. On tape 6 are written the time in seconds, the concentrations of electrons, O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, O<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>+</sup>, and the local time in hours. Tape 1 contains the time in seconds, the concentrations of NO<sup>+</sup>, NO, N,

$\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{O}$ , the value of the production function and the local time in hours. Tape 4 is the added auxiliary tape and contains the times in seconds, the concentrations of  $\text{O}_2$  and  $\text{N}_2$ , the settings of the KEY switches, the local time in hours, and the solar zenith angle in degrees.

### 7.2.1.3 The Solar Zenith Angle

The main program computes the angle of grazing incidence CIMAX which is the angle at the altitude in question between the zenith and the tangent to the earth.

$$\chi_{\max} = \pi - \sin^{-1} \left( \frac{R}{R+A} \right)$$

where  $R$  is the radius of the earth and  $A$  is the altitude. The sun is assumed to subtend an angle of  $0.5^\circ$ . Therefore, sunset first contact occurs when

$$\chi = \chi_{\max} - 0.25^\circ$$

and last contact occurs when

$$\chi = \chi_{\max} + 0.25^\circ$$

The solar zenith angle  $\chi$  is defined by

$$\cos \chi = \cos \delta \cos \phi \cos \theta + \sin \delta \sin \phi$$

From this the time in seconds corresponding to any zenith angle  $\chi$  is

$$t = \cos^{-1} \left\{ \frac{(\cos \chi - \sin \delta \sin \phi)}{\cos \delta \cos \phi} \right\} \cdot 1.3751 \times 10^4$$

During the daytime portion of the solution the code keeps the rate coefficients for photoattachment and photodissociation at fixed constants except for the  $\text{O}_2$  photodissociation which is computed according to the linear approximation previously discussed. During the nighttime portion of the solution, these rate constants are set to zero. During sunrise and sunset the rate coefficients for photoattachment and photodissociation are both increased or decreased according to the transmissivity percentage computed by the subprogram SUN.

The following statements, beginning on page 102, are a listing of the main program DIURN.

```

$IBFTC DIURN LIST
C DIURNAL VARIATION OF ATMOSPHERIC SPECIES AT ANY LATITUDE. DIUR0000
C SOLUTION OF THE REACTION RATE EQUATIONS IN THE IUNOSPHERE FOR 15 SPE DIUR0005
C IES AND WITH 168 REACTIONS. DIUR0010
C KB1=0 FOR LOG OUTPUT. DIUR0015
C KB1=1 FOR DECIMAL OUTPUT DIUR0020
C KB2=0 PRINTS HISTORY OF THE REACTIONS. DIUR0025
C KB2=1 DOES NOT PRINT HISTORY OF THE REACTIONS. DIUR0030
C KB3=0 PRINTS HISTORY AFTER EVERY SUCCESSFUL INTEGRATION. DIUR0035
C KB3=1 PRINTS HISTORY ONCE FOR EACH DECADE OF TIME. DIUR0040
C KB4=0 HALTS ON ERROR. DIUR0045
C KB4=1 READS ANOTHER POINT CARD AFTER AN ERROR. DIUR0050
C IPLOT=0 DOES NOT MAKE A PLOTTER TAPE. DIUR0055
C IPLOT=1 MAKES A LOG PLOTTER TAPE. DIUR0060
C B4=ALLOWABLE PERCENTAGE CHANGE IN PRODUCTION PER STEP. DIUR0065
C B6=NOONTIME LYMAN BETA O2 IONIZATION) DIUR0070
C B7=NOONTIME LYMAN ALPHA NO IONIZATION. DIUR0075
C B8 AND B9 ARE THE CONSTANTS FOR O2 PHOTODISSOCIATION APPROXIMATION DIUR0080
C RATE COEFFICIENT=B8-B9*CXI DIUR0085
C UNITS OF INPUT PARAMETERS ARE CGS. DIUR0090
C DIUR0095
C DIUR0100
COMMON TREG(150), UNZ(73), KEY(15), FORM(15), REMV(15), R(200), LKEY(15) DIUR0105
1), UO(73), CON(200), BEGIN(17), LOCK(15), XO2(73), XO(73), XN2(73), XNO( DIUR0110
273), XNE(73), ANGL(73), UO2(73), COB(10) DIUR0115
COMMON NUMB, EUBAR, ELBAR, D, DO2, CIMAX, DN2, T, PNE, PNO, PO2, PO, PN2, TOTA DIUR0120
1L, JAKE, JAM, ITER, ALT, LAM, TIME, KB3, ATIME, EAR, DTIME, CXI, SIND, COSD, JUG DIUR0125
2, TIMEX, ITEM, PXO2, PXO, PNX2, TOTO, TOTN, B6, B7, DEL, LINT, JACK, I2NT, K2NT, DIUR0130
3J2NT, N2NT, FIRST, IFAIL, JIP, B8, B9
DIMENSION DONT(20), TTREG(20), TITLE(12), HED(12), SIGM(30), IQ(30) DIUR0135
DIMENSION CRTNO(15), CRITN(15), A(168), B(168), C(168), G(168), ALF(7), ADIUR0140
11(69), A2(69), A3(30) DIUR0145
C DIUR0150
C DIUR0155
C THE FOLLOWING DATA ARE THE A, B, AND C'S FOR THE RATE CONSTANTS. DIUR0160
C DIUR0165
DATA A1/ 0.44E+00, 1.40E+00, 0.04E+00, 0.04E+00, 9.00E-15, 3.60E-16, DIUR0170
13.60E-16, 1.00E-13, 1.00E-13, 1.00E-13, 1.00E-13, 1.00E-13, 1.00E-13, DIUR0175
21.00E-13, 1.00E-13, 1.31E-15, 1.00E-19, 1.00E-17, 1.00E-17, 1.00E-11, DIUR0180
31.00E-11, 1.00E-31, 1.00E-31, 1.40E-31, 5.80E-33, 1.90E-33, 6.00E-28, DIUR0185
44.00E-29, 0.00E-00, 6.00E-05, 9.00E-05, 1.50E-04, 1.00E-24, 1.00E-22, DIUR0190
51.00E-22, 1.00E-22, 1.00E-23, 2.20E-10, 1.00E-12, 1.00E-12, 1.00E-12, DIUR0195
65.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, DIUR0200
75.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, 5.00E-07, DIUR0205
85.00E-07, 5.00E-07, 1.00E-23, 1.00E-23, 1.00E-23, 1.00E-23, 1.00E-23, DIUR0210
91.00E-23, 1.00E-23, 1.00E-23, 1.00E-23, 1.00E-23, 1.00E-23, 1.00E-11/ DIUR0215
DATA A2/ 1.00E-13, 1.00E-13, 0.00E-00, 1.00E-13, 1.00E-13, 1.00E-11, DIUR0220
11.00E-11, 1.00E-13, 0.00E-00, 1.00E-13, 1.00E-13, 1.00E-13, 1.00E-13, DIUR0225
24.00E-11, 2.40E-11, 0.00E-00, 0.00E-00, 8.00E-10, 1.00E-12, 1.00E-10, DIUR0230
30.00E-00, 5.00E-12, 1.00E-09, 1.00E-09, 1.00E-12, 1.00E-09, 1.00E-09, DIUR0235
41.00E-09, 1.00E-09, 1.00E-16, 1.00E-18, 0.00E-00, 0.00E-00, 0.00E-00, DIUR0240
50.00E-00, 0.00E-00, 1.00E-15, 1.00E-29, 1.00E-29, 0.00E-00, 0.00E-00, DIUR0245
60.00E-00, 0.00E-00, 0.00E-00, 1.00E-30, 1.00E-30, 3.00E-12, 3.00E-12, DIUR0250
73.00E-12, 1.00E-11, 1.80E-10, 1.00E-11, 2.50E-10, 1.00E-11, 1.00E-28, DIUR0255
81.00E-34, 1.00E-17, 1.00E-21, 1.00E-21, 2.00E-17, 1.00E-24, 6.40E-17, DIUR0260
91.00E-24, 1.00E-22, 1.00E-22, 5.00E-32, 2.00E-31, 5.00E-32, 3.20E-35/ DIUR0265
DATA A3/ 2.60E-35, 6.50E-34, 2.00E-31, 2.00E-33, 3.00E-33, 4.50E-33, DIUR0270
13.00E-30, 1.00E-33, 1.00E-33, 0.00E-00, 1.10E-10, 7.10E-17, 3.00E-11, DIUR0275
22.00E-10, 5.00E-11, 5.00E-10, 3.00E-16, 2.50E-11, 2.00E-13, 4.00E-12, DIUR0280
32.00E-11, 8.00E-13, 5.00E-06, 6.00E-08, 3.00E-03, 4.08E-07, 5.58E-08, DIUR0285

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```

DAY=1.0
NDAY=0
DIME=ATIME
IG0=1
TIMT=4.32E4
DO 35 J=1,150
35 TREG(J)=0.0
NUMB=15
L1NT=((2*NUMB)+4)
I2NT=((3*NUMB)+4)
K2NT=((4*NUMB)+4)
J2NT=((5*NUMB)+4)
N2NT=((6*NUMB)+4)
DO 40 J=1,NUMB
TIREG(J+3)=0.0
LOCK(J)=0
40 KEY(J)=1
DECO=DECL*0.01745329
CLA0=CLAT*0.01745329
COSD=COS(DECO)*COS(CLA0)
SIND=SIN(DECO)*SIN(CLA0)
CIMAX=3.1415926-ARSIN(EAR/(EAR+ALT))
CIMAD=57.295779*CIMAX
CIMID=ARCUS(SIND-COSD)
CIMAP=CIMAX-4.3633231E-3
CIMAT=CIMAX+4.3633231E-03
IF(CIMAP .GT. CIMID) GO TO 45
IF(CIMAT .LT. CIMID) GO TO 50
KSKP=3
GO TO 55
45 KSKP=1
GO TO 65
50 KSKP=2
C TIM IS SECONDS FROM ZENITH TO CIMAP (NOON TO SUNSET FIRST CONTACT).
55 TIM=ARCOS((COS(CIMAP)-SIND)/COSD)*1.3750987E4
IF(KSKP .EQ. 3) GO TO 60
TOM=ARCOS((COS(CIMAT)-SIND)/COSD)*1.3750987E4
DARK=8.64E4-2.0*TOM
60 SILLY=TIM+4.32E4
65 CALL INITAL
C COMPUTE RATE CONSTANTS IN THE FORM K=A*(T**B)*EXP(-C/T)
C
K=1
DO 70 J=1,69
A(K)=A1(J)
70 K=K+1
DO 75 J=1,69
A(K)=A2(J)
75 K=K+1
DO 80 J=1,30
A(K)=A3(J)
80 K=K+1
DO 85 J=1,NOCOM
85 CON(J)=A(J)*(T**B(J))*EXP(-C(J)/T)
C
DO 90 J=1,4
90 COB(J)=CON(J)
M=161
DO 95 J=5,10
DIUR0585
DIUR0590
DIUR0595
DIUR0600
DIUR0605
DIUR0610
DIUR0615
DIUR0620
DIUR0625
DIUR0630
DIUR0635
DIUR0640
DIUR0645
DIUR0650
DIUR0655
DIUR0660
DIUR0665
DIUR0670
DIUR0675
DIUR0680
DIUR0685
DIUR0690
DIUR0695
DIUR0700
DIUR0705
DIUR0710
DIUR0715
DIUR0720
DIUR0725
DIUR0730
DIUR0735
DIUR0740
DIUR0745
DIUR0750
DIUR0755
DIUR0760
DIUR0765
DIUR0770
DIUR0775
DIUR0780
DIUR0785
DIUR0790
DIUR0795
DIUR0800
DIUR0805
DIUR0810
DIUR0815
DIUR0820
DIUR0825
DIUR0830
DIUR0835
DIUR0840
DIUR0845
DIUR0850
DIUR0855
DIUR0860
DIUR0865
DIUR0870
DIUR0875

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	COB(J)=CON(M)	DIUR0880
95	M=M+1	DIUR0885
C	PREPARE OUTPUT TAPES AND WRITE RATE CONSTANTS AND INITIAL	DIUR0890
C	CONDITIONS.	DIUR0895
	WRITE(6,635) ALT,D,T	DIUR0900
	WRITE(6,650) DECL,CLAT,CIMAD	DIUR0905
	WRITE(6,700)	DIUR0910
	IS=1	DIUR0915
	DO 100 J=1,15	DIUR0920
	IT=IS+5	DIUR0925
	WRITE(6,685) (I,A(I),I=IS,IT)	DIUR0930
	WRITE(6,705) (I,CON(I),I=IS,IT)	DIUR0935
	IS=IS+5	DIUR0940
100	CONTINUE	DIUR0945
	WRITE(6,735)	DIUR0950
	DO 105 J=1,13	DIUR0955
	IT=IS+5	DIUR0960
	WRITE(6,685) (I,A(I),I=IS,IT)	DIUR0965
	WRITE(6,705) (I,CON(I),I=IS,IT)	DIUR0970
	IS=IS+6	DIUR0975
105	CONTINUE	DIUR0980
	WRITE(6,645)	DIUR0985
	ATIM=ATIME/3600.0	DIUR0990
	IF(KB1 .EQ. 0) GO TO 110	DIUR0995
	WRITE(6,730) TREG(2),(TREG(J),J=4,11),ATIM	DIUR1000
	WRITE(1) TREG(2),(TREG(J),J=12,18),TOTAL,ATIM	DIUR1005
	MOUNT=MOUNT+1	DIUR1010
	GO TO 145	DIUR1015
110	M=NUMB+3	DIUR1020
	DO 125 J=2,M	DIUR1025
	DEC=TREG(J)	DIUR1030
	IF(DEC) 580,115,120	DIUR1035
115	DONT(J)=0.0	DIUR1040
	GO TO 125	DIUR1045
120	DONT(J)=ALOG10(DEC)	DIUR1050
125	CONTINUE	DIUR1055
	IF(TOTAL) 580,130,135	DIUR1060
130	DPROD=0.0	DIUR1065
	GO TO 140	DIUR1070
135	DPROD=ALOG10(TOTAL)	DIUR1075
140	WRITE(6,730) DONT(2),(DONT(J),J=4,11),ATIM	DIUR1080
	WRITE(1) DONT(2),(DONT(J),J=12,18),DPROD,ATIM	DIUR1085
	MOUNT=MOUNT+1	DIUR1090
145	IF(TREG(3) .LT. 1.8E3) GO TO 150	DIUR1095
	TREG(3)=9.0E2	DIUR1100
150	GO TO (155,160,235),KSKP	DIUR1105
155	TESS=8.46E4*DAY	DIUR1110
	IF(ATIME .LT. TESS) GO TO 265	DIUR1115
	DAY=DAY+1.0	DIUR1120
	NDAY=NDAY+1	DIUR1125
	GO TO 265	DIUR1130
160	TESS=ATIME+TREG(3)	DIUR1135
	IF(TESS-SILLY) 265,180,165	DIUR1140
165	GO TO (170,185,185,205,215,215),JIP	DIUR1145
170	TREG(3)=(SILLY-ATIME)	DIUR1150
175	JIP=2	DIUR1155
	GO TO 265	DIUR1160
180	GO TO (175,175,210,210),JIP	DIUR1165
		DIUR1170

```

185 CXI=ARCOS(COSD*COS(7.2722052E-5*(ATIME+4.32E4))+SIND)
    IF(CXI .GT. CIMAT) GO TO 190
    IF(TREG(3) .LT. 10.0) GO TO 265
    TREG(3)=10.0
    JIP=3
    GO TO 265
190 SILLY=SILLY+DARK
    DO 195 J=1,4
195 CON(J)=0.0
    DO 200 J=161,166
200 CON(J)=0.0
    JIP=4
    NDAY=NDAY+1
    GO TO 265
205 TREG(3)=(SILLY-ATIME)
210 JIP=5
    GO TO 265
215 CXI=ARCOS(COSD*COS(7.2722052E-5*(ATIME+4.32E4))+SIND)
    IF(CXI .LT. CIMAP) GO TO 220
    IF(TREG(3) .LT. 10.0) GO TO 265
    TREG(3)=10.0
    JIP=6
    GO TO 265
220 SILLY=SILLY+(8.46E4-DARK)
    JIP=1
    DO 225 J=1,4
225 CON(J)=A(J)*(T*B(J))*EXP(-C(J)/T)
    DO 230 J=161,166
230 CON(J)=A(J)*(T*B(J))*EXP(-C(J)/T)
    GO TO 265
235 TESS=ATIME+TREG(3)
    IF(TESS-SILLY) 265,245,240
240 GO TO (245,255,250),JIP
245 TREG(3)=(SILLY-ATIME)
    JIP=2
    GO TO 265
250 CXI=ARCOS(COSD*COS(7.2722052E-5*(ATIME+4.32E4))+SIND)
    IF(CXI .LT. CIMAP) GO TO 260
    IF(TREG(3) .LT. 10.0) GO TO 265
    TREG(3)=10.0
    JIP=3
    GO TO 265
260 SILLY=SILLY+8.46E4
    JIP=1
265 DO 270 K=1,NUMB
    IF(KEY(K)-2) 275,270,270
270 CONTINUE
    CALL ALGA
    TREG(3)=2.0*TREG(3)
    TREG(2)=TREG(2)+TREG(3)
    GO TO 300
C
C   INTEGRATION OF EQUATIONS STARTS HERE.
C
275 CALL INTEG
    GO TO(300,280,300,300,290,300),JIP
280 IF(IFAIL) 285,300,285
285 JIP=1
    GO TO 300

```

```

DIUR1175
DIUR1180
DIUR1185
DIUR1190
DIUR1195
DIUR1200
DIUR1205
DIUR1210
DIUR1215
DIUR1220
DIUR1225
DIUR1230
DIUR1235
DIUR1240
DIUR1245
DIUR1250
DIUR1255
DIUR1260
DIUR1265
DIUR1270
DIUR1275
DIUR1280
DIUR1285
DIUR1290
DIUR1295
DIUR1300
DIUR1305
DIUR1310
DIUR1315
DIUR1320
DIUR1325
DIUR1330
DIUR1335
DIUR1340
DIUR1345
DIUR1350
DIUR1355
DIUR1360
DIUR1365
DIUR1370
DIUR1375
DIUR1380
DIUR1385
DIUR1390
DIUR1395
DIUR1400
DIUR1405
DIUR1410
DIUR1415
DIUR1420
DIUR1425
DIUR1430
DIUR1435
DIUR1440
DIUR1445
DIUR1450
DIUR1455
DIUR1460
DIUR1465

```



```

290 IF(IFAIL) 295,300,295
295 JIP=4
300 CALL BALAN
    ATIME=ATIME+(TREG(3)/2.0)
    CHID=57.295779*CXI
    IF(TREG(3) .NE. 2.0E-6) GO TO 305
    KLOT=KLOT+1
    IF(KLOT .GT. 10) GO TO 310
305 KLOT=0
    ATIM=ATIME/3600.0
    GO TO 315
310 WRITE(6,690)
    GO TO 585
315 IF(KB1 .NE. 0) GO TO 320
    DDO2=ALOG10(DO2)
    DDN2=ALOG10(DN2)
    WRITE(4) DONT(2),DDO2,DDN2,(KEY(J),J=1,NUMB),ATIM,CHID
    GO TO 325
320 WRITE(4) TREG(2),DO2,DN2,(KEY(J),J=1,NUMB),ATIM,CHID
325 KOUNT=KOUNT+1
    DO 330 J=1,NUMB
330 LKEY(J)=KEY(J)
    K=JAKE
    GO TO (335,570,575),K
335 JACK=2
    KIND=1
    CALL SLOP(KIND)
    KIND=2
    CALL SLOP(KIND)
    N2=LINT
    DO 340 I=1,NUMB
    CRTN(I)=2.0*ABS((TREG(N2)-TREG(I+3))/TREG(3))
    CRTNO(I)=REMV(I)*TREG(I+3)
    N2=N2+1
340 CONTINUE
    CRTNO(10)=CRTNO(10)+PNO
    CRTNO(15)=CRTNO(15)+PO
    DO 360 J=1,NUMB
    IF(CRTN(J) .GT. 1.0E-3) GO TO 345
    IF(ABS(1.0-(FORM(J)/CRTNO(J))) .GT. DEL) GO TO 350
345 IF(CRTNO(J) .EQ. 0.0) GO TO 360
    IF((CRTN(J)/CRTNO(J)) .LT. DEL) GO TO 355
350 LOCK(J)=0
    GO TO 360
355 LOCK(J)=LOCK(J)+1
360 CONTINUE
    DO 380 J=1,NUMB
    IF(KEY(J)-3) 365,380,380
365 IF(LOCK(J)-3) 370,375,375
370 KEY(J)=1
    GO TO 380
375 KEY(J)=2
380 CONTINUE
    JACK=2
    DO 385 J=1,NUMB
    IF(KEY(J) .GT. 3) GO TO 385
    IF(TREG(J+3) .GT. TTREG(J+3)) GO TO 385
    IF(TREG(J+3) .GT. CHI) GO TO 385
    KEY(J)=3

```

```

DIUR1470
DIUR1475
DIUR1480
DIUR1485
DIUR1490
DIUR1495
DIUR1500
DIUR1505
DIUR1510
DIUR1515
DIUR1520
DIUR1525
DIUR1530
DIUR1535
DIUR1540
DIUR1545
DIUR1550
DIUR1555
DIUR1560
DIUR1565
DIUR1570
DIUR1575
DIUR1580
DIUR1585
DIUR1590
DIUR1595
DIUR1600
DIUR1605
DIUR1610
DIUR1615
DIUR1620
DIUR1625
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DIUR1645
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DIUR1655
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DIUR1665
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DIUR1675
DIUR1680
DIUR1685
DIUR1690
DIUR1695
DIUR1700
DIUR1705
DIUR1710
DIUR1715
DIUR1720
DIUR1725
DIUR1730
DIUR1735
DIUR1740
DIUR1745
DIUR1750
DIUR1755
DIUR1760

```

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```
TREG(J+3)=0.0
385 CONTINUE
   IF(PNE) 405,390,405
390 IF((TREG(4)/BEGIN(1))-1.0E-3) 395,405,405
395 DO 400 J=1,3
   TREG(J+3)=0.0
400 KEY(J)=3
405 DO 410 J=1,NUMB
410 TTREG(J+3)=TREG(J+3)

   OUTPUT OF RESULTS STARTS HERE.

   IF(KNT=50) 420,415,415
415 WRITE(6,645)
   KNT=0
420 KNT=KNT+1
   ATIM=ATIME/3600.0
   IF(KBI .EQ. 0) GO TO 425
   WRITE(6,730) TREG(2),(TREG(J),J=4,11),ATIM
   WRITE(1) TREG(2),(TREG(J),J=12,18),TOTAL,ATIM
   GO TO 460
425 K=NUMB+3
   DO 440 J=2,K
   DEC=TREG(J)
   IF(DEC) 580,430,430
430 DONT(J)=0.0
   GO TO 440
435 DONT(J)=ALOG10(DEC)
440 CONTINUE
   IF(TOTAL) 580,445,450
445 TOTL=0.0
   GO TO 455
450 TOTL=ALOG10(TOTAL)
455 WRITE(6,730) DONT(2),(DONT(J),J=4,11),ATIM
   WRITE(1) DONT(2),(DONT(J),J=12,18),TOTL,ATIM
460 CALL PLOT(IPLT)
   MOUNT=MOUNT+1
465 IF(ATIME-TIMT) 475,470,470
470 TIMT=TIMT+4.32E4
   CALL DAUXT
```

DECISION TO CONTINUE INTEGRATION OR STOP IS MADE HERE.

```
475 IF(TREG(2) .LT. 1.0) GO TO 500
   GO TO (480,485),IGO
480 IGO=2
   SAVE=TREG(2)
   ICNT=1
   GO TO 500
485 IF(ICNT .GT. 50) GO TO 490
   ICNT=ICNT+1
   GO TO 500
490 IF((TREG(2)-SAVE) .GT. 1.0) GO TO 495
   WRITE(6,710)
   GO TO 585
495 IGO=1
500 IF(TREG(4) .LT. ENDE) GO TO 585
505 IF(ATIM .GT. ENDR) GO TO 585
```

DIUR1765  
DIUR1770  
DIUR1775  
DIUR1780  
DIUR1785  
DIUR1790  
DIUR1795  
DIUR1800  
DIUR1805  
DIUR1810  
DIUR1815  
DIUR1820  
DIUR1825  
DIUR1830  
DIUR1835  
DIUR1840  
DIUR1845  
DIUR1850  
DIUR1855  
DIUR1860  
DIUR1865  
DIUR1870  
DIUR1875  
DIUR1880  
DIUR1885  
DIUR1890  
DIUR1895  
DIUR1900  
DIUR1905  
DIUR1910  
DIUR1915  
DIUR1920  
DIUR1925  
DIUR1930  
DIUR1935  
DIUR1940  
DIUR1945  
DIUR1950  
DIUR1955  
DIUR1960  
DIUR1965  
DIUR1970  
DIUR1975  
DIUR1980  
DIUR1985  
DIUR1990  
DIUR1995  
DIUR2000  
DIUR2005  
DIUR2010  
DIUR2015  
DIUR2020  
DIUR2025  
DIUR2030  
DIUR2035  
DIUR2040  
DIUR2045  
DIUR2050  
DIUR2055

C	TEST SYSTEM CLOCK FOR IMMINENT TIMER OVERFLOW.	DIUR2060
C		DIUR2065
	510 CALL CLOCK	DIUR2070
	CALL SLITET(4,K000FX)	DIUR2075
	GO TO (515,520),K000FX	DIUR2080
	515 ILK=2	DIUR2085
	GO TO 585	DIUR2090
	520 BIG=AMAX1(TREG(4),TREG(5),TREG(6),TREG(7),TREG(8))	DIUR2095
	DO 525 J=1,5	DIUR2100
	IF(BIG .EQ. TREG(J+3)) GO TO 530	DIUR2105
	525 CONTINUE	DIUR2110
	530 IF(J-LAM) 535,540,535	DIUR2115
	535 KEY(LAM)=1	DIUR2120
	JACK=1	DIUR2125
	540 LAM=J	DIUR2130
	KEY(LAM)=4	DIUR2135
	STOT=TOTAL	DIUR2140
	545 TREG(2)=TREG(2)+TREG(3)	DIUR2145
	CALL PRODUK	DIUR2150
	TREG(2)=TREG(2)-TREG(3)	DIUR2155
	IF(TOTAL-STOT) 550,145,555	DIUR2160
	550 RATIO=STOT/TOTAL	DIUR2165
	GO TO 560	DIUR2170
	555 RATIO=TOTAL/STOT	DIUR2175
	560 IF(RATIO-B4) 145,145,565	DIUR2180
	565 TREG(3)=TREG(3)/2.0	DIUR2185
	GO TO 545	DIUR2190
C		DIUR2195
C	ERROR COMMENT OUTPUTS.	DIUR2200
C		DIUR2205
	570 WRITE(6,660) TREG(2)	DIUR2210
	GO TO 585	DIUR2215
	575 WRITE(6,665) TREG(2)	DIUR2220
	GO TO 585	DIUR2225
	580 WRITE(6,655)	DIUR2230
	K=NUMB+3	DIUR2235
	WRITE(6,670) (TREG(J),J=2,K),TOTAL	DIUR2240
	585 IF(KB4 .EQ. 1) GO TO 590	DIUR2245
	KB6=2	DIUR2250
C		DIUR2255
C	TRANSFER ALL RESULTS TO OUTPUT TAPE HERE.	DIUR2260
C		DIUR2265
	590 REWIND 1	DIUR2270
	END FILE 3	DIUR2275
	IF(IPLOT .NE. 1) GO TO 600	DIUR2280
	END FILE 0	DIUR2285
	REWIND 8	DIUR2290
	DO 595 K=1,ITEM	DIUR2295
	READ(8)SIGM(1),IQ(1),(SIGM(J),IQ(J),J=10,18)	DIUR2300
	WRITE(0,750)SIGM(1),IQ(1),(SIGM(J),IQ(J),J=10,18)	DIUR2305
	595 CONTINUE	DIUR2310
	END FILE 0	DIUR2315
	REWIND 8	DIUR2320
	600 KNT=0	DIUR2325
	WRITE(6,695)	DIUR2330
	DO 605 K=1,MOUNT	DIUR2335
	READ(1) TREG(2),(TREG(J),J=12,18),TOTAL,ATIM	DIUR2340
	WRITE(6,730) TREG(2),(TREG(J),J=12,18),TOTAL,ATIM	DIUR2345
	KNT=KNT+1	DIUR2350

```

IF(KNT .LT. 50) GO TO 605
WRITE(6,695)
KNT=0
605 CONTINUE
REWIND 1
REWIND 4
KNT=0
WRITE(6,720)
DO 610 K=1,KOUNT
READ(4) TREG(2),O2,DN2,(KEY(J),J=1,NUMB),ATIM,CHID
WRITE(6,715) TREG(2),O2,DN2,(KEY(J),J=1,NUMB),ATIM,CHID
KNT=KNT+1
IF(KNT .LT. 50) GO TO 610
WRITE(6,720)
KNT=0
610 CONTINUE
REWIND 4
GO TO (5,615),IB6
615 REWIND 3
REWIND 0
CALL EXIT
C
620 FORMAT(1P5E14.7)
625 FORMAT(1P6E12.5)
630 FORMAT(94H1 SOLUTION OF THE REACTION RATE EQUATIONS WITH 15 SPECIES
1 AND 168 REACTIONS DIURNAL VARIATION. )
635 FORMAT(11H ALTITUDE =1PE11.4,4H CM.,17H TOTAL DENSITY =1PE12.5,15H
1H TEMPERATURE =OP57.2)
640 FORMAT(14)
645 FORMAT(121H1 TIME (SEC) N(E) /CC N(O-) /CC N(O2-) /CC NDI
1(O3-) /CC N(NO2-) /CC N(O+) /CC N(O2+) /CC N(N2+) /CC TID
2E(HOUR) )
650 FORMAT(20H0 SOLAR DECLINATION =1PE13.5,10H DEGREES. ,6X10H LATITUDE
1=OPF6.2,10H DEGREES. ,6X20H ANGLE OF GRAZING INCIDENCE =1PE13.5,10H
2 DEGREES. )
655 FORMAT(65H0 THE PROGRAM IN TRYING TO GENERATE THE LOG OF A NEGATIVE
1 NUMBER. )
660 FORMAT(45H0 THE INTEGRATING MESH IS VANISHING IN INT AT 1PE11.5,6H
1 SEC. )
665 FORMAT(47H0 THE INTEGRATING MESH IS VANISHING IN ALGA AT 1PE11.5,6H
1H SEC. )
670 FORMAT(1P10E10.2)
675 FORMAT(12A6)
680 FORMAT(1H0,12A6)
685 FORMAT(1H0,(6(2X4H A(,13,2H)=1PE10.3)))
690 FORMAT(43H THE INCREMENT IS CONSTANT AT 1.0E-06 SEC. )
695 FORMAT(130H1 TIME (SEC) N(NO+) /CC N(NO) /CC N(N) /CC
1N(N2) /CC N(O3) /CC N(N2O) /CC N(O) /CC PRODUCTION TIME
2E(HOUR) )
700 FORMAT(22H0 REACTION COEFFICIENTS)
705 FORMAT(1H ,(5(2X4H CONI,13,2H)=1PE10.3))
710 FORMAT(60H TIME IS NOT INCREASING RAPIDLY ENOUGH TO ADVANCE SOLUT
1DN. )
715 FGRMAT(1P3E13.5,15I4,1PE13.5,OPF11.5)
720 FORMAT(121H1 TIME (SEC) O2 DENSITY N2 DENSITY E O- O2- O3
1- NO2- O+ O2+ N2+ NO+ NO N NO2 O5 N2O O TIME(HOUR) CHI
2)
725 FORMAT(14,1PE10.2,OPF5.1,1PE10.2,7A6)
730 FORMAT(1P10E13.5)
735 FORMAT(1H1)
740 FORMAT(12A6)
745 FORMAT(5I2)
750 FORMAT(6X11(A1,15))
755 FORMAT(1H0,20X,86H THE FOLLOWING IS A LIST OF RATE CONSTANT CHANGES
1 FROM THE STD LIST USED IN THIS RUN. )
760 FORMAT(1H1,12A6)
END
DIUR2355
DIUR2360
DIUR2365
DIUR2370
DIUR2375
DIUR2380
DIUR2385
DIUR2390
DIUR2395
DIUR2400
DIUR2405
DIUR2410
DIUR2415
DIUR2420
DIUR2425
DIUR2430
DIUR2435
DIUR2440
DIUR2445
DIUR2450
DIUR2455
DIUR2460
DIUR2465
DIUR2470
DIUR2475
DIUR2480
DIUR2485
DIUR2490
DIUR2495
DIUR2500
DIUR2505
DIUR2510
DIUR2515
DIUR2520
DIUR2525
DIUR2530
DIUR2535
DIUR2540
DIUR2545
DIUR2550
DIUR2555
DIUR2560
DIUR2565
DIUR2570
DIUR2575
DIUR2580
DIUR2585
DIUR2590
DIUR2595
DIUR2600
DIUR2605
DIUR2610
DIUR2615
DIUR2620
DIUR2625
DIUR2630
DIUR2635
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DIUR2645
DIUR2650
DIUR2655
DIUR2660
DIUR2665
DIUR2670
DIUR2675
DIUR2680
DIUR2685

```

## 7.2.2 THE PHOTOIONIZATION PRODUCTION SUBROUTINE PRODUC

Upon being called by SLOP or the main program, PRODUC first computes the solar zenith angle for the time at which it was called. Using this zenith angle, the subroutine performs a table look-up in the photoionization rate tables read into the computer by the main program. If the computed zenith angle is not a tabular value, linear interpolations are performed in the tables to obtain the proper production rates for the positive ions.

One-tenth of one percent of the noontime production rate of  $O_2^+$  by  $L_\beta$  is automatically added to the computed production rate of  $O_2^+$ . One percent of the noontime production rate of  $NO^+$  by  $L_\alpha$  is always added to the production rate of  $NO^+$ . These production rates are added in order to allow a certain amount of these radiations to scatter into the nighttime atmosphere.

After the production rates for all the positive ions are computed, they are summed to obtain the production rate of the electrons.

The following statements are a listing of this subroutine.

```

$IBFTC PRODUC LIST
SUBROUTINE PRODUC
C THIS SUBROUTINE COMPUTES THE PRODUCTION FROM THE Q TABLES.
C
COMMON TREG(150), UN2(73), KEY(15), FORM(15), REMV(15), R(200), LKEY(15)
1) UO(73), CON(200), BEGIN(17), LOCK(15), XO2(73), XO(73), XN2(73), XNO(73)
273), XNE(73), ANGL(73), UO2(73), COB(10)
COMMON NUMB, EUBAR, ELBAR, D, DO2, CIMAX, DN2, T, PNE, PNO, PO2, PO, PN2, TOTAPROD
1L, JAKE, JAM, ITER, ALT, LAM, TIME, KB3, ATIME, EAR, DTIME, CXI, SIND, COSD, JUGPROD
2, TIMEX, ITEM, PXO2, PXO, PXN2, TOTO, TOTN, 86, 87, DEL, LINT, JACK, J2NT, K2NT,
3J2NT, N2NT, FIRST, IFALL, JIP, R8, B9
TIMEX=DTIME +TREG(2)
CXI=ARCOS(COSD*COS(7.2722052E-5*(TIMEX+4.32E4))+SIND)
DO 5 J=1,73
IF(CXI-ANGL(J)).15,10,5
5 CONTINUE
10 PO2=UO2(J)
PO=UO(J)
PN2=UN2(J)
PXO2=XO2(J)
PXO=XO(J)
PXN2=XN2(J)
PNO=XNO(J)*TREG(13)
GO TO 20
15 PART=(ANGL(J-1)-CXI)/(ANGL(J-1)-ANGL(J))
PO2=UO2(J-1)+PART*(UO2(J)-UO2(J-1))
PO=UO(J-1)+PART*(UO(J)-UO(J-1))
PN2=UN2(J-1)+PART*(UN2(J)-UN2(J-1))
PXO2=XO2(J-1)+PART*(XO2(J)-XO2(J-1))
PXO=XO(J-1)+PART*(XO(J)-XO(J-1))
PXN2=XN2(J-1)+PART*(XN2(J)-XN2(J-1))
PNO=XNO(J-1)+PART*(XNO(J)-XNO(J-1))
PNO=PNO*TREG(13)
20 QT=(1.0E-16*D)/(DO2+DN2)
PNO=PNO+87*1.0E-02
PO2=PO2+QT*DO2+PXO2+1.0E-03*B6
PN2=PN2+QT*DN2+PXN2
PO=PO+PXO
PNE=PO2+PO+PN2+PNO
TOTAL=PNE
RETURN
END
PROD0000
PROD0005
PROD0010
PROD0015
PROD0020
PROD0025
PROD0030
PROD0035
PROD0040
PROD0045
PROD0050
PROD0055
PROD0060
PROD0065
PROD0070
PROD0075
PROD0080
PROD0085
PROD0090
PROD0095
PROD0100
PROD0105
PROD0110
PROD0115
PROD0120
PROD0125
PROD0130
PROD0135
PROD0140
PROD0145
PROD0150
PROD0155
PROD0160
PROD0165
PROD0170
PROD0175
PROD0180
PROD0185
PROD0190
PROD0195
PROD0200
PROD0205

```

## 7.2.3 THE CHARGE BALANCE SUBROUTINE BALAN

This subroutine computes the largest . . . re species from charge balance and adjusts the O<sub>2</sub> and N<sub>2</sub> concentrations to . . . ure conservation of O and N atoms. In addition to this it also calls subrouthi SUN if the solution has advanced into a sunrise or sunset period. Subrcutine SUN returns with a transmissivity percentage by which subroutine BALAN multiplies the photodetachment and photo-dissociation rate coefficients. The solution has arrived at a period of sunrise or sunset if switch JIP is on three or six respectively. Switch JIP is set by the main program.

The following statements are a listing of this subprogram.

```

$IBFTC BALAN LIST
SUBROUTINE BALAN
COMMON TREG(150),UN2(73), KEY(15),FORM(15),REHV(15),R(200),LKEY(15)
1),UD(73), CON(200),BEGIN(17),LOCK(15),XO2(73),XO(73),XN2(73),XNO(73)
273),XNE(73),ANGL(73),UG2(73),COB(10)
COMMON NUMB,EUBAR,ELBAR,D,DO2,CIMAX,DN2,T, PNE,PNO,PO2,PO,PN2,TOTABALN
1L,JAKE,JAM,ITER,ALT,LAM,TIME,KB3,ATIME,EAR,DTIME,CXI,SIND,COSD,JUGBALN
2,TIMEX,ITEM,PXO2,PXO,PXN2,TOTO,TOTN,86,87,DEL,LINT,JACK,I2NT,K2NT,
3J2NT,N2NT,FIRST,IFAIL,JIP,88,89
5 SUM=TREG(9)+TREG(10)+TREG(11)+TREG(12)
GO TO (10,15,20,25,30,35),LAM
10 TREG(4)=SUM-TREG(5)-TREG(6)-TREG(7)-TREG(8)
GO TO 35
15 TREG(5)=SUM-TREG(4)-TREG(6)-TREG(7)-TREG(8)
GO TO 35
20 TREG(6)=SUM-TREG(4)-TREG(5)-TREG(7)-TREG(8)
GO TO 35
25 TREG(7)=SUM-TREG(4)-TREG(5)-TREG(6)-TREG(8)
GO TO 35
30 TREG(8)=SUM-TREG(4)-TREG(5)-TREG(6)-TREG(7)
35 DO2=((TOTO-TREG(5)-3.0*TREG(7)-TREG(9)-TREG(12)-3.0*TREG(15)-TREG(
116)-TREG(17)-TREG(18))/2.0)-TREG(6)-TREG(8)-TREG(10)-TREG(14)
DN2=((TOTN-TREG(8)-TREG(12)-TREG(13)-TREG(14)-TREG(16))/2.0)-TREG(
111)-TREG(17)
TIMEX=DTIME +TREG(2)
CXI=ARCCOS(COSD*COS(7.2722052E-5*(TIMEX+4.32E4))+SIND)
COB(5)=88-89*CXI
IF(COB(5)) 40,45,45
40 COB(5)=0.0
45 GO TO (65,65,50,65,65,50),JIP
50 FRACT=SUN(CXI,CIMAX)
AT=FRACT
DO 55 J=1,4
55 CON(J)=COB(J)*FRACT
N=161
DO 60 J=5,10
CON(N)=COB(J)*FRACY
60 N=N+1
GO TO 70
65 CON(161)=COB(5)
70 RETURN
END
BALN0000
BALN0005
BALN0010
BALN0015
BALN0020
BALN0025
BALN0030
BALN0035
BALN0040
BALN0045
BALN0050
BALN0055
BALN0060
BALN0065
BALN0070
BALN0075
BALN0080
BALN0085
BALN0090
BALN0095
BALN0100
BALN0105
BALN0110
BALN0115
BALN0120
BALN0125
BALN0130
BALN0135
BALN0140
BALN0145
BALN0150
BALN0155
BALN0160
BALN0165
BALN0170
BALN0175
BALN0180
BALN0185
BALN0190
BALN0195
BALN0200
BALN0205

```

## 7.2.4 SUBROUTINE SUN

Being given the value of the solar zenith angle and the value of C<sub>MAX</sub>, this subroutine when called by BALAN computes the transmission factor for use in changing the rate coefficients for photodetachment and photodissociation.

The following statements are a listing of the FORTRAN statements for this subroutine.

\$IBFTC SUN	LIST	SUN00000
	FUNCTION SUN(CHI,ALPHA)	SUN00005
C		SUN00010
C	TO COMPUTE ETA AS A FUNCTION OF CHI.	SUN00015
C		SUN00020
	DATA GAMMA/4.3033231E-3/	SUN00025
	X=(CHI-(ALPHA-GAMMA))/GAMMA	SUN00030
	IF(X) 5,10,10	SUN00035
5	X=0.0	SUN00040
	GO TO 20	SUN00045
10	IF(X-2.0) 20,20,15	SUN00050
15	X=2.0	SUN00055
20	THETA=ARCOS((2.0*((1.0-X)**2))-1.0)	SUN00060
	IF(X-1.0) 30,25,25	SUN00065
25	THETA=(6.28318531-THETA)	SUN00070
30	A=(THETA/2.0)-((1.0-X)*SQRT((1.0-COS(THETA))/2.0))	SUN00075
	SUN=1.0-(A/3.1415926)	SUN00080
	IF(SUN .LT. 0.0) GO TO 40	SUN00085
	IF(SUN .GT. 1.0) GO TO 35	SUN00090
	GO TO 45	SUN00095
35	SUN=1.0	SUN00100
	GO TO 45	SUN00105
40	SUN=0.0	SUN00110
45	RETURN	SUN00115
	END	SUN00120

### Acknowledgments

The author wishes to express his gratitude to Dr. Wolfgang Pfister for his continued keen interest in this problem and for his many helpful discussions and recommendations. Thanks are also extended to Ronald J. Fowler for his ideas and help in modifying the code especially as it applies to the diurnal variation and other applications not presented here. The assistance of Miss Margaret Gardner of Boston College in executing the code and in preparing the results for presentation here is also greatly appreciated.

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## Appendix A

### The Photoionization Production Function Program

As discussed in Section 5.1, there is a separate code for the computation of the photoionization production function tables. This code consists of three programs; the main program, subroutine PRODUC, and subroutine COLUM. The output from this code is a listing and a deck of 145 cards containing the number of ions produced as a function of the zenith angle for a given altitude and geographic location. This is the deck of cards that is required as part of the input to the diurnal variation code.

The main program simply controls the input and output of this code. A considerable amount of input is required in order to compute the photoionization functions for each of the species ionized. This information is read into the computer by Cards Nos. 40 through 100 of the main program. The input consists of the photoionization and absorption cross sections for O, O<sub>2</sub>, and N<sub>2</sub>; the flux in photons/cm<sup>2</sup>/sec of the incident solar radiation at the top of the atmosphere; the hard X-ray flux and absorption cross sections for air for these X-rays; and the neutral atmosphere profiles from 0 to 520 km of O, O<sub>2</sub>, and N<sub>2</sub>. These parameters, as taken from Tables 1 and 2, are read in the following order into the designated regions.

A2

SPO2 = 45 values of the photoionization cross section of  $O_2$  .

SO2 = 45 values of the total absorption cross section of  $O_2$  .

SPO = 34 values of the photoionization cross section of  $O$  .

SO = 34 values of the total absorption cross section of  $O$  .

SPN2 = 24 values of the photoionization cross section of  $N_2$  .

SN2 = 24 values of the total absorption cross section of  $N_2$  .

PHI = values of the solar flux in photons/cm<sup>2</sup>/sec broken down into 24 lines or bands.

RAD = the X-ray flux at 2, 4, and 8A.

ABC = absorption cross section for air at 2, 4, and 8A.

These parameters are punched on cards in FORMAT (1P6E12.5):

CONO = the height profile of  $O$  in number/cm<sup>3</sup> at every 10 km.

CONO2 = the height profile of  $O_2$  in number/cm<sup>3</sup> at every 10 km.

CONN2 = the height profile of  $N_2$  in number/cm<sup>3</sup> at every 10 km.

The last three parameters are punched on cards in FORMAT (1P9E8.2).

The main program sets up the BK region with values of altitude in 10 km increments from 0 to 520 km for ease of table look-up of required concentrations. The concentrations as read into the computer are converted into the corresponding common logarithms since it is more realistic to linearly interpolate the logs of the densities rather than the concentrations themselves whenever a nontabular value is required.

After all of these basic parameters are read into the computer, the parameters of the altitude and the geographic location are read in. Each altitude card is preceded by a title card on which 72 columns of hollerith information may be punched. The information on this title card is punched out on a heading card preceding the cards containing the photoionization functions. The second card of this set of two contains the following parameters punched in FORMAT (1P6E12.5).

HITE = altitude in km at which the functions are required.

EPSI = the  $L_{\alpha}$  flux at the top of the atmosphere in ergs/cm<sup>2</sup>/sec.

EAR = radius of the earth in km.

DECL = solar declination in degrees.

CLAT = latitude in degrees.

The printed output consists of the following:

- a) the altitude, solar declination, and latitude;
- b) the solar zenith angle and the number of seconds after noon, corresponding to this zenith angle;
- c)  $\int_z^{520} M \, dl$ ,  $\int_z^{520} N(O_2) \, dl$ ,  $\int_z^{520} N(N_2) \, dl$ , and  $\int_z^{520} N(O) \, dl$  ;
- d) the production rate of  $O_2$ ,  $O$ , and  $N_2$  by X-rays in the wavelength region  $<170\text{\AA}$  and the rate coefficient for the ionization of NO by  $L_\alpha$ ;
- e) the production rate of  $O_2$ ,  $O$ , and  $N_2$  by UV at wavelengths  $>170\text{\AA}$ ;
- f) the production rate of  $O_2$  and  $N_2$  by cosmic rays; and
- g) the total production rates by X-rays, UV, and cosmic rays.

The punched output consists of the following:

- a) a title card which is a duplicate of the title card read into the computer; and,
- b) a deck of 145 cards containing the production functions.

There are two cards for one set of values of these functions. A set is computed for every ten minutes from noon to midnight. It is assumed that the values from midnight to noon are the same as these.

The parameters which are punched in FORMAT (1P5E14.7, 2X, I3, 2X, I3) are as follows:

- a) SQ2 = total UV production rate of  $O_2^+$ ;
- b) SQO = total UV production rate of  $O^+$ ;
- c) SQN2 = total UV production rate of  $N_2^+$ ;
- d) QNO = rate coefficient for production of  $NO^+$  by ionization of NO by  $L_\alpha$ ;
- e) WHOLE = total production rate of electrons except for  $L_\alpha$  ionization;
- f) IHTE = altitude of computations;
- g) KARDS = card sequence number;
- h) CIII = solar zenith angle;
- i) SXO2 = production rate of  $O_2^+$  by X-rays;
- j) SXO = production rate of  $O^+$  by X-rays;

A4

- k) SNX2 = production rate of  $N_2^+$  by X-rays; and,
- l) SCRAY = total cosmic ray production.

The following statements, beginning on page A5, are a listing of the main program.

Subroutine PRODUC computes the actual production rate of each of the species using the input data and the equations derived in Section 5.1. The following statements, beginning on page A7, are a listing of this code.

Subroutine COLUM computes the number of particles in a  $cm^2$  column along a ray path at a given solar zenith angle and extending from the height  $z$  to 520 km. An upper limit of the 520 km was chosen because for paths that extend down to the D and E regions particle concentrations above 520 km do not contribute significantly to the total integral. The subroutine exits with the values of the following integrals in the corresponding locations.

$$DEPTH = \int M \, dl$$

$$DEPO_2 = \int N(O_2) \, dl$$

$$DEPO = \int N(O) \, dl$$

$$DEPN2 = \int N(N_2) \, dl .$$

The following statements, beginning on page A9, are a listing of the FORTRAN statements for this subroutine.

```

$IBFTC MAIN LIST MAIN0000
C PHOTOIONIZATION SOURCE FUNCTION MAIN0005
COMMON SPO2(45),SO2(45),SPO(45),SO(45),SPN2(45),SN2(45),PHI(24),RAMAIN0010
10(3),QO2(27),QO(27),QN2(27),ABC(3),BK(150),CONT(150),CONO2(150),COMAIN0015
2NN2(150),CONO(150),CONTL(150),CONO2L(150),CONN2L(150),CONOL(150) MAIN0020
COMMON DEPO2,DEPN2,DEPTH,SQO2,S'QO,SQN2,QNO,CO2,CN2,EPSI,R,HITE,CHIMAIN0025
1,CIMIN,DO2,DN2,OO,D,ONO,EAR,SXC1,SXO,SXN2,KLAW,DEPO MAIN0030
DIMENSION TITLE(12) MAIN0035
READ(5,85)(SPO2(J),J=1,45) MAIN0040
READ(5,85)(SO2(J),J=1,45) MAIN0045
READ(5,85)(SPO(J),J=12,45) MAIN0050
READ(5,85)(SO(J),J=12,45) MAIN0055
READ(5,85)(SPN2(J),J=22,45) MAIN0060
READ(5,85)(SN2(J),J=1,45) MAIN0065
READ(5,85)(PHI(J),J=1,24) MAIN0070
READ(5,85)(RAD(J),J=1,3) MAIN0075
READ(5,85)(ABC(J),J=1,3) MAIN0080
READ(5,65)(CONO(J),J=1,52) MAIN0085
READ(5,65)(CONO2(J),J=1,52) MAIN0090
READ(5,65)(CONN2(J),J=1,52) MAIN0095
BK(1)=0.0 MAIN0100
DO 5 J=2,52 MAIN0105
5 BK(J)=BK(J-1)+10.0 MAIN0110
DO 10 J=1,52 MAIN0115
10 CONT(J)=CONO(J)+CONO2(J)+CONN2(J) MAIN0120
DO 15 J=1,52 MAIN0125
CONTL(J)=ALOG10(CONT(J)) MAIN0130
CONOL(J)=ALOG10(CONO(J)) MAIN0135
CONO2L(J)=ALOG10(CONO2(J)) MAIN0140
15 CONN2L(J)=ALOG10(CONN2(J)) MAIN0145
20 READ(5,80)(TITLE(J),J=1,12) MAIN0150
READ(5,85)HITE,EPSI,B,EAR,DECL,CLAT MAIN0155
IF(HITE) 60,60,25 MAIN0160
25 WRITE(6,70)HITE,DECL,CLAT MAIN0165
KOUNT=0 MAIN0170
KARDS=0 MAIN0175
IHITE=HITE MAIN0180
WRITE(7,80)(TITLE(J),J=1,12) MAIN0185
DO 30 J=1,51 MAIN0190
IF(HITE-BK(J)) 35,35,30 MAIN0195
30 CONTINUE MAIN0200
35 RATY=(HITE-BK(J-1))/10.0 MAIN0205
DO1=10.0**((CONO2L(J-1)+RATY*(CONO2L(J)-CONO2L(J-1))) MAIN0210
DN2=10.0**((CONN2L(J-1)+RATY*(CONN2L(J)-CONN2L(J-1))) MAIN0215
DO=10.0**((CONOL(J-1)+RATY*(CONOL(J)-CONOL(J-1))) MAIN0220
D=10.0**((CONTL(J-1)+RATY*(CONTL(J)-CONTL(J-1))) MAIN0225
DECR=DECL*0.01745329 MAIN0230
CLAR=CLAT*0.01745329 MAIN0235
COSD=COS(DECL)*COS(CLAR) MAIN0240
SIND=SIN(DECL)*SIN(CLAR) MAIN0245
TYM=0.0 MAIN0250
CIMIN=3.1415926-ARSIN(EAR/(EAR+HITE)) MAIN0255
40 CHI=ARCOS(COSD*COS(7.2722052E-5*TYM)+SIND) MAIN0260
CHID=57.295779*CHI MAIN0265
WRITE(6,75)CHID,TYM MAIN0270
CALL PRODUK MAIN0275
WRITE(6,110)DEPTH,DEPO2,DEPN2,DEPO MAIN0280
SXRAY=SXO2+SXN2+SXO MAIN0285
SUV=SQO2+SQO+SQN2 MAIN0290

```

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```
SCRAY=C02+CN2
WHOLE=SXRAY+SUV+SCRAY
WRITE(6,90)SX02,SX0,SXN2,QNO
WRITE(6,95)SQ02,SG0,SQN2
WRITE(6,105)C02,CN2
WRITE(6,100)SXRAY,SUV,SCRAY,WHOLE
WRITE(7,115)SQ0?,SQ0,SQN2,QNO,WHOLE,IHITE,KARDS
KARDS=KARDS+1
WRITE(7,115)CHI,SX02,SX0,SXN2,SCRAY,IHITE,KARDS
KARDS=KARDS+1
KOUNT=KOUNT+8
IF(KOUNT-56)50,45,45
45 KOUNT=0
WRITE(6,70)HITE,DECL,CLAT
50 IF(8)60,55,20
55 TYM=TYM+6.0E2
IF(TYM-4.32E4)40,40,20
60 CALL EXIT
65 FORMAT(1P9E8.2)
70 FORMAT(13H1 ALTITUDE =1PE13.5,4H CM.,6X19HSOLAR DECLINATION =1PE13.5,10H DEGREES. ,6X10HLATITUDE =1PE13.5,10H DEGREES )
75 FORMAT(15H0ZENITH ANGLE =F7.2,10H DEGREES. ,18H TIME AFTER NOON =,
11PE11.3,6H SEC. )
80 FORMAT(12A6)
85 FORMAT(1P6E12.5)
90 FORMAT(1H ,15H02+ FROM XRAYS=1PE12.5,3X,14H0+ FROM XRAYS=1PE12.5,3X,15HN2+ FROM XRAYS=1PE12.5,3X,21HN0+ CGEFFICIENT =1PE12.5)
95 FORMAT(1H ,15H02+ FROM UV =1PE12.5,3X,14H0+ FROM UV =1PE12.5,3X,15HN2+ FROM UV =1PE12.5)
100 FORMAT(17H XRAY ELECTRONS =1PE12.5,17H UV ELECTRONS =1PE12.5,25H COSMIC RAY ELECTRONS =1PE12.5,20H TOTAL ELECTRONS =1PE12.5)
105 FORMAT(16H 02+ COSMIC RAY=1PE12.5,32X15HN2+ COSMIC RAY=1PE12.5)
110 FORMAT(18H0 TOTAL INTEGRAL =1PE13.5,14H 02 INTEGRAL =E13.5,14H N2 INTEGRAL =E13.5,13H 0 INTEGRAL =E13.5)
115 FORMAT(1P5E14.7,2X,13,2X,13)
END
```

```
MAIN0295
MAIN0300
MAIN0305
MAIN0310
MAIN0315
MAIN0320
MAIN0325
MAIN0330
MAIN0335
MAIN0340
MAIN0345
MAIN0350
MAIN0355
MAIN0360
MAIN0365
MAIN0370
MAIN0375
MAIN0380
MAIN0385
MAIN0390
MAIN0395
MAIN0400
MAIN0405
MAIN0410
MAIN0415
MAIN0420
MAIN0425
MAIN0430
MAIN0435
MAIN0440
MAIN0445
MAIN0450
MAIN0455
MAIN0460
MAIN0465
MAIN0470
```

```

$IBFTC PRODUC LIST
SUBROUTINE PRODUC
C
C PHOTOIONIZATION PRODUCTION FUNCTION
C
COMMON SPO2(45),SO2(45),SPD(45),SO(45),SPN2(45),SN2(45),PHI(24),RAPROD0025
1D(3),QO2(27),QO(27),QN2(27),ABC(3),BK(150),CONT(150),CONO2(150),COPROD0030
2NN2(150),CONO(150),CONTL(150),CONO2L(150),CONN2L(150),CONOL(150) PROD0035
COMMON DEPO2,DEPN2,DEPTH,SQO2,SQO,SN2,QNO,CO2,CN2,EPSI,R,HITE,CHIPROD0040
1,CIMIN,DO2,ON2,DU,O,DNO,EAR,SXO2,SXO,SN2,KLAW,DEPO PROD0045
DIMENSION POWER(45) PROD0050
DO 5 J=1,27 PROD0055
QO2(J)=0.0 PROD0060
QO(J)=0.0 PROD0065
5 QN2(J)=0.0 PROD0070
SQO2=0.0 PROD0075
SQO=0.0 PROD0080
SN2=0.0 PROD0085
QNO=0.0 PROD0090
SXO2=0.0 PROD0095
SN2=0.0 PROD0100
SXO=0.0 PROD0105
IF(CHI-CIMIN) 10,10,130 PROD0110
10 CALL COLUM PROD0115
DO 15 J=1,45 PROD0120
15 POWER(J)=EXP(-DEPO2*SO2(J)-DEPO*SO(J)-DEPN2*SN2(J)) PROD0125
DO 20 J=1,6 PROD0130
20 QO2(J)=SPO2(J)*DO2*PHI(J)*POWER(J) PROD0135
K=7 PROD0140
K1=11 PROD0145
K2=1 PROD0150
DO 50 J=7,9 PROD0155
25 PART1=SPO2(K)*DO2*PHI(J) PROD0160
PART2=SPO(K)*DO*PHI(J) PROD0165
QO2(J)=QO2(J)+(PART1*POWER(K)) PROD0170
QO(J)=QO(J)+(PART2*POWER(K)) PROD0175
IF(K-K1) 30,35,35 PROD0180
30 K=K+1 PROD0185
GO TO 25 PROD0190
35 K=K+1 PROD0195
GO TO (40,45,55),K2 PROD0200
40 K1=16 PROD0205
K2=2 PROD0210
GO TO 50 PROD0215
45 K1=21 PROD0220
K2=3 PROD0225
50 CONTINUE PROD0230
55 K1=24 PROD0235
K2=1 PROD0240
DO 80 J=10,11 PROD0245
60 PART1=SPO2(K)*DO2*PHI(J) PROD0250
PART2=SPO(K)*DO*PHI(J) PROD0255
PART3=SPN2(K)*ON2*PHI(J) PROD0260
QO2(J)=QO2(J)+(PART1*POWER(K)) PROD0265
QO(J)=QO(J)+(PART2*POWER(K)) PROD0270
QN2(J)=QN2(J)+(PART3*POWER(K)) PROD0275
IF(K-K1) 65,70,70 PROD0280
65 K=K+1 PROD0285
GO TO 60 PROD0290

```



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```
70 K=K+1
GO TO (75,80),K2
75 K1=27
K2=2
80 CONTINUE
QO2(12)=SPO2(28)*DO2*PHI(12)*POWER(K)
QO(12)=SPO(28)*DO*PHI(12)*POWER(K)
QN2(12)=SPN2(28)*DN2*PHI(12)*POWER(K)
K=29
K1=31
K2=1
DO 105 J=13,14
85 PART1=SPO2(K)*DO2*PHI(J)
PART2=SPO(K)*DO*PHI(J)
PART3=SPN2(K)*DN2*PHI(J)
QO2(J)=QO2(J)+(PART1*POWER(K))
QO(J)=QO(J)+(PART2*POWER(K))
QN2(J)=QN2(J)+(PART3*POWER(K))
IF(K-K1) 90,95,95
90 K=K+1
GO TO 85
95 K=K+1
GO TO (100,105),K2
100 K1=34
K2=2
105 CONTINUE
QO2(15)=SPO2(35)*DO2*PHI(15)*POWER(K)
QO(15)=SPO(35)*DO*PHI(15)*POWER(K)
QN2(15)=SPN2(35)*DN2*PHI(15)*POWER(K)
QO2(16)=(DO2*PHI(16))*(SPO2(36)*POWER(36)+SPO2(37)*POWER(37))
QO(16)=(DO*PHI(16))*(SPO(36)*POWER(36)+SPO(37)*POWER(37))
QN2(16)=DN2*PHI(16)*(SPN2(36)*POWER(36)+SPN2(37)*POWER(37))
K=38
DO 110 J=17,24
QO2(J)=SPO2(K)*DO2*PHI(J)*POWER(K)
QO(J)=SPO(K)*DO*PHI(J)*POWER(K)
QN2(J)=SPN2(K)*DN2*PHI(J)*POWER(K)
110 K=K+1
L=1
DO 115 J=25,27
QO2(J)=DO2*RAD(L)*EXP(-(DEPTH*ABC(L)))
QO(J)=DO*RAD(L)*0.75*EXP(-(DEPTH*ABC(L)))
QN2(J)=DN2*RAD(L)*EXP(-(DEPTH*ABC(L)))
L=L+1
115 CONTINUE
DO 120 J=1,18
SQO2=SQO2+QO2(J)
SQN2=SQN2+QN2(J)
120 SQO=SQO+QO(J)
DO 125 J=19,27
SXO2=SXO2+QO2(J)
SXN2=SXN2+QN2(J)
125 SXO=SXO+QO(J)
QNO=EPSI*1.34E-7*EXP(-8.5E-21*DEPO2)
130 QT=(1.0E-16*D)/(DO2+DN2)
CO2=QT*QO2
CN2=QT*QN2
135 RETURN
END
```

```
PROD0295
PROD0300
PROD0305
PROD0310
PROD0315
PROD0320
PROD0325
PROD0330
PROD0335
PROD0340
PROD0345
PROD0350
PROD0355
PROD0360
PROD0365
PROD0370
PROD0375
PROD0380
PROD0385
PROD0390
PROD0395
PROD0400
PROD0405
PROD0410
PROD0415
PROD0420
PROD0425
PROD0430
PROD0435
PROD0440
PROD0445
PROD0450
PROD0455
PROD0460
PROD0465
PROD0470
PROD0475
PROD0480
PROD0485
PROD0490
PROD0495
PROD0500
PROD0505
PROD0510
PROD0515
PROD0520
PROD0525
PROD0530
PROD0535
PROD0540
PROD0545
PROD0550
PROD0555
PROD0560
PROD0565
PROD0570
PROD0575
PROD0580
PROD0585
```

```

$IBFTC COLUM LIST
SUBROUTINE COLUM
COMMON SPO2(45),SO2(45),SPO(45),SO(45),SPN2(45),SN2(45),PHI(24),RACOLM0000
10(3),QO2(27),QO(27),QN2(27),ABC(3),BK(150),CONT(150),CONO2(150),COCOLM0005
2NN2(150),CONO(150),CONL(150),CONO2L(150),CONN2L(150),CONOL(150) COLM0010
COMMON DEPG2,DEPN2,DEPTH,SQO2,SQO,SON2,QNO,CO2,CN2,EPST,R,HITE,CHICOLM0015
1,CIMIN,DO2,DN2,DO,D,DNO,EAR, SXO2,SXO, SXN2,KLA, DEPO COLM0020
DIMENSION ANS(4),A(4),A2(4),ANSL(4),A3(4),ANSQ(4),PDT(4),ANSW(4) COLM0025
C
DO 5 I=1,4
A2(I)=0.
5 A3(I)=0.
TEN=10.0
DEGRA=0.5236
P=0.0
Q=0.0
KUTY=0
KUTD=4
10 TEST=10
15 BETAR=(EAR+HITE)
BETAR=3.1415926-CHI
IF(BETAR-ARSIN(EAR/UTOR)) 20,30,30
20 WRITE(6,25)
25 FORMAT(34H0THIS PATH GOES BELOW THE HORIZON )
GO TO 230
30 COSB=COS(BETAR)
DISTR=0.
BUTR2= UTOR**2
YUR=2.0* UTOR*COSB
IF(HITE-95.0) 40,35,35
35 IF(CHI-1.5707963) 45,45,40
40 KUTY=1
KUTD=3
45 HTOR=(SQRT(BUTR2+(DISTR**2)-(DISTR*YUR)))- EAR
50 DO 65 J=1,101
IF(BK(J)-HTOR) 65,55,90
55 ANS(1)=CONT(J)
ANS(2)=CONO2(J)
ANS(3)=CONN2(J)
IF(KUTY) 100,60,100
60 ANS(4)=CONO(J)
GO TO 100
65 CONTINUE
IF(Q) 70,80,70
70 DO 75 I=1,KUTD
A2(I)=A2(I)-ANSL(I)
A3(I)=A3(I)-ANSQ(I)
75 ANSW(I)=ANSQ(I)
GO TO 145
80 DO 85 I=1,KUTD
A3(I)=A3(I)-ANSQ(I)
85 ANSW(I)=ANSQ(I)
GO TO 145
90 TLAZY=(HTOR-BK(J-1))/10.0
ANS(1)=10.0**((CONL(J-1)+(TLAZY*(CONL(J)-CONL(J-1))))
ANS(2)=10.0**((CONO2L(J-1)+(TLAZY*(CONO2L(J)-CONO2L(J-1))))
ANS(3)=10.0**((CONN2L(J-1)+(TLAZY*(CONN2L(J)-CONN2L(J-1))))
IF(KUTY) 100,95,100
95 ANS(4)=10.0**((CONOL(J-1)+(TLAZY*(CONOL(J)-CONOL(J-1))))
COLM0030
COLM0035
COLM0040
COLM0045
COLM0050
COLM0055
COLM0060
COLM0065
COLM0070
COLM0075
COLM0080
COLM0085
COLM0090
COLM0095
COLM0100
COLM0105
COLM0110
COLM0115
COLM0120
COLM0125
COLM0130
COLM0135
COLM0140
COLM0145
COLM0150
COLM0155
COLM0160
COLM0165
COLM0170
COLM0175
COLM0180
COLM0185
COLM0190
COLM0195
COLM0200
COLM0205
COLM0210
COLM0215
COLM0220
COLM0225
COLM0230
COLM0235
COLM0240
COLM0245
COLM0250
COLM0255
COLM0260
COLM0265
COLM0270
COLM0275
COLM0280
COLM0285
COLM0290

```

K10

```
100 IF(P) 115,105,115
105 DO 110 I=1,KUTO
110 A(I)=ANS(I)
    P=1.0
    GO TO 140
115 IF(Q) 130,120,130
120 DO 125 I=1,KUTO
    A2(I)=ANS(I)+A2(I)
125 ANSL(I)=ANS(I)
    Q=1.0
    GO TO 140
130 DO 135 I=1,KUTO
    A3(I)=ANS(I)+A3(I)
135 ANSQ(I)=ANS(I)
    Q=0.0
140 DISTR=DISTR+TEST
    GO TO 45
145 DO 150 I=1,KUTO
150 POT(I)=[(TEST*1.0E5)/3.0]*((A(I)+ANSW(I))+(4.0*A2(I))+(2.0*A3(I)))
    DEPTH=POT(I)
    DEPO2=POT(2)
    DEPN2=POT(3)
    IF(KUYI) 160,155,160
155 DEPO=POT(4)
    GO TO 230
160 P=0.0
    Q=0.0
    DISTR=0.0
165 HTOR=SQRT(BUTR2+(DISTR**2)-(DISTR*YUR))- EAR
    DO 175 J=1,51
    IF(BK(J)-HTOR) 175,170,165
170 ANS(4)=CONO(J)
    GO TO 200
175 CONTINUE
    IF(Q) 180,190,180
180 A2(4)=A2(4)-ANSL(4)
    A3(4)=A3(4)-ANSQ(4)
    ANSW(4)=ANSQ(4)
185 DEPO=1.666667E5*((A(4)+ANSW(4))+(4.0*A2(4))+(2.0*A3(4)))
    GO TO 230
190 A3(4)=A3(4)-ANSQ(4)
    ANSW(4)=ANSQ(4)
    GO TO 185
195 TLAZY=(HTOR-BK(J-1))/10.0
    ANS(4)=10.0*(CONOL(J-1)+TLAZY*(CONOL(J)-CONOL(J-1)))
200 IF(P) 210,205,210
205 A(4)=ANS(4)
    P=1.0
    GO TO 225
210 IF(Q) 220,215,220
215 A2(4)=ANS(4)+A2(4)
    ANSL(4)=ANS(4)
    Q=1.0
    GO TO 225
220 A3(4)=ANS(4)+A3(4)
    ANSQ(4)=ANS(4)
    Q=0.0
225 DISTR=DISTR+5.0
    GO TO 165
230 RETURN
    END
```

COLM0295  
COLM0300  
COLM0305  
COLM0310  
COLM0315  
COLM0320  
COLM0325  
COLM0330  
COLM0335  
COLM0340  
COLM0345  
COLM0350  
COLM0355  
COLM0360  
COLM0365  
COLM0370  
COLM0375  
COLM0380  
COLM0385  
COLM0390  
COLM0395  
COLM0400  
COLM0405  
COLM0410  
COLM0415  
COLM0420  
COLM0425  
COLM0430  
COLM0435  
COLM0440  
COLM0445  
COLM0450  
COLM0455  
COLM0460  
COLM0465  
COLM0470  
COLM0475  
COLM0480  
COLM0485  
COLM0490  
COLM0495  
COLM0500  
COLM0505  
COLM0510  
COLM0515  
COLM0520  
COLM0525  
COLM0530  
COLM0535  
COLM0540  
COLM0545  
COLM0550  
COLM0555  
COLM0560  
COLM0565  
COLM0570  
COLM0575  
COLM0580  
COLM0585  
COLM0590  
COLM0595

## Appendix B

### The Differential Equation Writer Program

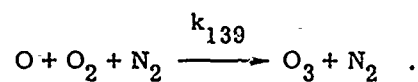
This code was originally written by David McIntyre (1965) for computing the total derivative of each species with respect to time and the partial derivatives of each species with respect to the other species. His code was written for an IBM-6000 computer, so in order to use this code on an IBM-7044 or 7094 computer it had to be rewritten. The author has made the modifications necessary for computing the codes for the formation sums  $\sum F_i$  and the removal sums  $\sum R_i$ . The code consists of a main program and eight subroutines; DIFFEQ, SET8, DY, REFACT, DIFFER, FACTOR, OUT, CODER, and DECODE. Because the last two subprograms involve character manipulations that are not easily performed in the FORTRAN language, they are written in the MAP language.

The main program essentially controls the input and output. The input consists of a deck of cards containing the reactions in coded form. The output is a listing and a deck of cards containing the FORTRAN statements for subroutine SLOP. The only thing that has to be added to the deck is the proper COMMON statement. For the system described in this report, the following code applies. Since all of the species listed after the total density are not considered in the program, there is no output code for them.

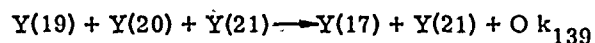
B2

Species	Input to Program	Output From Program	Species	Input to Program	Output From Program
e	5	Y(1)	N <sub>2</sub> O	18	Y(14)
O <sup>-</sup>	6	Y(2)	O	19	Y(15)
O <sub>2</sub> <sup>-</sup>	7	Y(3)	O <sub>2</sub>	20	Y(16)
O <sub>3</sub> <sup>-</sup>	8	Y(4)	N <sub>2</sub>	21	Y(17)
NO <sub>2</sub> <sup>-</sup>	9	Y(5)	Total Density	22	Y(18)
O <sup>+</sup>	10	Y(6)	N <sup>+</sup>	23	----
O <sub>2</sub> <sup>+</sup>	11	Y(7)	NO <sub>3</sub> <sup>+</sup>	24	----
N <sub>2</sub> <sup>+</sup>	12	Y(8)	N <sub>2</sub> O <sup>+</sup>	25	----
NO <sup>+</sup>	13	Y(9)	O <sub>3</sub> <sup>+</sup>	26	----
NO	14	Y(10)	NO <sub>3</sub>	27	----
N	15	Y(11)	N <sub>4</sub> <sup>+</sup>	28	----
NO <sub>2</sub>	16	Y(12)	NO <sub>2</sub> <sup>+</sup>	29	----
O <sub>3</sub>	17	Y(13)	NO <sup>-</sup>	30	----

The reactions are punched on cards in coded form in FORMAT (20I4). Consider the reaction



This reaction is coded as



and punched as

bb19bb20bb21bb17bb21bbb0b139.

Each reaction must contain seven integers: three for the reactants, three for the products, and one for the reaction number. If a reaction contains less than three reactants or less than three products the corresponding subfields must contain zeros.

The output is a complete FORTRAN deck from the \$IBFTC card to the END card with the exception of a COMMON statement. Although the subroutine is a general one, it still requires a COMMON statement compatible with the remainder of the code in which it is used. The following statements, beginning on page B4, are a listing of the main program.

Subroutine SET8 is called by the main program and assigns an identification to each of the reactions according to type. This is a digit from one to seven and is added to the coded reaction as the eighth integer. The maximum type of reaction that this program can handle is a three-reactant three-product process. The type identifiers as related to the reactions are shown in the comments of the FORTRAN program. The following statements, beginning on page B6, are a listing of subprogram SET8.

Subroutine DY scans the reactions searching for a particular species as a reactant or a product. If it finds the species as a reactant it transfers the reactants to the IREMOV region. The memory cell preceding the cells containing the reactants is coded as -2 if the reaction type is one, as -3 if the reaction type is two, three, or four, and as -4 if the reaction type is five, six, or seven. If it finds the species as a product it transfers the reactants to the IFORM region. Now the memory cell preceding the cells containing the reactants is coded as described above except that the sign of the digit is positive.

Upon a normal exit from this subroutine, all of the reactants for processes that form a particular species are in the IFORM region and all of the reactants for processes that remove this species are in the IREMOV region.

The following statements, beginning on page B7, are a listing of subroutine DY.

Subroutine DIFFER computes the partial derivatives of each differential equation with respect to the species for which the equation was written. Effectively, this routine factors out the given species from all the reactions that remove it so that the quantity  $\sum R_i$  can be computed. The following statements, beginning on page B8, are a listing of this program.

Subroutine REFACT performs the factoring of species and leaves the reactions in the IFACT region in as highly a factored form as possible. The following statements, beginning on page B9, are a listing of the FORTRAN statements for this subprogram.

Subroutine FACTOR which is called very often by subroutine REFACT does the actual factoring. It scans a particular series of reactions set up by REFACT to find the species occurring most often in the series. It factors out this species and returns to REFACT with the factored version of the series fed to it by REFACT. The following statements, beginning on page B11, are a listing of this subroutine.

B4

```
$IBFTC DIFG LIST
COMMON OUTPUT(2000)
DIMENSION IREAC(8,200),IPART(500),INSERT(500),IFACT(500),ICUR(500) DIFQ0005
1,INSTIK(500),IIOLT(500),IFORM(500),IREMV(500) DIFQ0010
DIMENSION ID(2000),C(5) DIFQ0015
DATA Q/6H+PNE ,6H+POZ ,6H+PU ,6H+PNZ ,6H+PNO-
READ(5,110) NEQNS,NSPEC1
READ(5,5) ((IREAC(I,J),I=1,7),J=1,NEQNS) DIFQ0035
5 FORMAT(2014) DIFQ0040
WRITE(6,90) DIFQ0045
PUNCH 115
NO=1
N1=2
CALL SET8(IREAC,NEQNS) DIFQ0065
JSTOP=NSPEC1+4 DIFQ0070
DO 80 J=5,JSTOP DIFQ0075
ICUR(1)=1001 DIFQ0080
IMARK=2 DIFQ0085
IPOINT=1 DIFQ0090
ICOUNT=0 DIFQ0095
CALL DYIJ,NEQNS,IREAC,IFORM,IREMV,ISPEAR,LENDY DIFQ0100
LDEN=J DIFQ0105
CALL DIFFER(IREPV,LENDY,LDEN,IPART,LIPART,LFLAG,ICUR(IMARK),LICUR) DIFQ0110
IMARK=IMARK+LICUR DIFQ0115
JI=J-4 DIFQ0120
LDENC=LDEN-4 DIFQ0125
IF(LIPART)10,30,10 DIFQ0130
10 INSERT(IPOINT)=J DIFQ0135
INSERT(IPOINT+1)=LDEN DIFQ0140
INSERT(IPOINT+2)=LDEN DIFQ0145
15 IPOINT=IPOINT+3 DIFQ0150
ICOUNT=ICOUNT+1 DIFQ0155
C DIFQ0160
C PUT PARENTHESIS AROUND IPART DIFQ0165
DO 20 I=1,LIPART DIFQ0170
II=LIPART-I+1 DIFQ0175
20 IPART(II+1)=IPART(II) DIFQ0180
IPART(LIPART+2)=-1001 DIFQ0185
IPART(1)=1001 DIFQ0190
LENGIP=LIPART+2 DIFQ0195
CALL REFACT(IPART,NSPEC1,IFACT,LENGIP) DIFQ0200
CALL OUT(IFACT,LENGIP,IAKROW) DIFQ0205
DO 21 JJD=1,2000
21 ID(JJD)=0 DIFQ0210
CALL DECODE(OUTPUT,ID,IARROW,INUMB) DIFQ0215
WRITE(6,95) NO,LDENC,LDENC,N1 DIFQ0225
PUNCH 95, NO,LDENC,LDENC,N1
WRITE(6,25) LDENC,(ID(I),I=1,INUMB)
PUNCH 25, LDENC,(ID(I),I=1,INUMB)
25 FORMAT(6X,5HREPV(,12,5H),9A6/(5X,1H1,11A6)) DIFQ0235
C DIFQ0240
C PUT PARENTHESIS AROUND IDYJOT DIFQ0245
30 CU 35 I=1,ISPEAR DIFQ0250
II=ISPEAR-I+1 DIFQ0255
35 IFGRM(II+1)=IFORM(II) DIFQ0260
IFORM(ISPEAR+2)=-1001 DIFQ0265
IFORM(1)=1001 DIFQ0270
LENGIH=ISPEAR+2 DIFQ0275
```

CALL REFACT(IFORM,ASPECI,IFACT,LENGTH)	DIFQ0280
CALL OUT(IFACT,LENGTH,IARROW)	DIFQ0285
DO 36 JJC=1,2000	
36 ID(JJC)=0	
IF(J .EQ. 5) GO TO 40	DIFQ0290
IF(J .EQ. 13) GO TO 45	DIFQ0295
IF(J .EQ. 12) GO TO 50	DIFQ0300
IF(J .EQ. 14) GO TO 55	DIFQ0305
IF(J .EQ. 15) GO TO 60	DIFQ0310
GO TO 65	DIFQ0315
40 IARRG=IARRC+1	DIFQ0320
OUTPLT(IARRC)=Q(1)	
GO TO 65	DIFQ0335
45 IARRC=IARRC+1	DIFQ0340
OUTPLT(IARRC)=C(2)	
GO TO 65	DIFQ0355
50 IARROW=IARRC+1	DIFQ0360
OUTPUT(IARRC)=Q(2)	
GO TO 65	DIFQ0375
55 IARRG=IARROW+1	DIFQ0380
OUTPUT(IARROW)=L(4)	
GO TO 65	DIFQ0395
60 IARROW=IARROW+1	DIFQ0400
OUTPLT(IARROW)=C(5)	
65 CALL DECCDE(OUTPLT, ID, IARROW, INUMB)	DIFQ0415
J1=J-4	DIFQ0420
70 WRITE(6,75) J1,(IC(I),I=1,INUMB)	DIFQ0425
PUNCH 75, J1,(ID(I),I=1,INUMB)	
75 FORMAT(6X,5HFURM(,12,5H) ,9A0/(5X,1H1,11A6))	DIFQ0435
NO=N1	DIFQ0440
N1=N0+1	DIFQ0445
80 CONTINUE	DIFQ0450
WRITE(6,100) NO	DIFQ0455
PUNCH 100,NO	
WRITE(6,105)	DIFQ0465
PUNCH 105	
85 STOP	DIFQ0475
90 FORMAT(19H11BFTC SLOP LIST/6X,21HSUBROUTINE SLOP(KIND)/6X,23HD1DIFQ0480	
1MENSION Y(250),C(173)/6X,34HEQUIVALENCE (Y(1),TREG(4)),(C,CON)/5X,	
2 11H CALL BALAN/6X,9HY(19)=DU2/6X,9HY(20)=DN2/6X,7HY(21)=D/6X,2	
33HIF(KIND .EQ. 2) GO TO 1/6X,11HCALL PRODC)	
95 FORMAT(1H ,14,27H IF(KIND .EQ. 1 .AND. KEY(,12,38H) .NE. 1) .OK. DIFQ0500	
1(KIND .EQ. 2 .AND. KEY(/5X,1H1,12,17H) .NE. 2)) GO TO ,13) DIFQ0505	
100 FORMAT(1H ,14,7H RETURN)	DIFQ0510
105 FORMAT(6X,3HEND)	DIFQ0515
110 FORMAT(214)	
115 FORMAT(19H11BFTC SLOP LIST/6X,21HSUBROUTINE SLOP(KIND)/6X,23HD1DIFQ0480	
1MENSION Y(250),C(173)/6X,34HEQUIVALENCE (Y(1),TREG(4)),(C,CON)/5X,	
2 11H CALL BALAN/6X,9HY(19)=DU2/6X,9HY(20)=DN2/6X,7HY(21)=D/6X,2	
33HIF(KIND .EQ. 2) GO TO 1/6X,11HCALL PRODC)	
END	DIFQ0520



\$IBFTC SET8	LIST	SET80000
	SUBROUTINE SET8(I,REAC,NEQNS)	SET80005
C		SET80010
C	SUBROUTINE IDENTIFIES THE TYPE OF EACH REACTION AND LOADS IREAC(8,K)	SET80015
C	WITH THE TYPE NO. FOR EACH EQUATION K=1,2,...,NEQNS L.T. 200.	SET80020
C	TYPE 1 I GOES TO J + K	SET80025
C	TYPE 2 I + J GOES TO K	SET80030
C	TYPE 3 I + J GOES TO K + L	SET80035
C	TYPE 4 I + J GOES TO K + L+M	SET80040
C	TYPE 5 I + J + K GOES TO L	SET80045
C	TYPE 6 I + J + K GOES TO L + M	SET80050
C	TYPE 7 I + J + K GOES TO L + M +N	SET80055
	DIMENSION IREAC(8,200)	SET80060
	DO 40 II=1,NEQNS	SET80065
	LMARK=0	SET80070
	IRIGHT=0	SET80075
	DO 10 IPT=1,3	SET80080
	IF(I,IREAC(IPT,II))10,5,10	SET80085
	5 LMARK=LMARK+1	SET80090
	10 CONTINUE	SET80095
	DO 20 IF=4,6	SET80100
	IF(I,IREAC(IF,II))20,15,20	SET80105
	15 IRIGHT=IRIGHT+1	SET80110
	20 CONTINUE	SET80115
	IF(LMARK-1)35,30,25	SET80120
	25 IREAC(8,II)=1	SET80125
	GO TO 40	SET80130
	30 IREAC(8,II)=4-IRIGHT	SET80135
	GO TO 40	SET80140
	35 IREAC(8,II)=7-IRIGHT	SET80145
	40 CONTINUE	SET80150
	RETURN	SET80155
	END	SET80160

```

$IBFTC DY      LIST
SUBROUTINE DY(J,NEQNS,IAC,IFORM,IEMOV,ISPEAR,IARROW)
DIMENSION IAC(8,200),IFORM(500),IEMOV(500)
C IFORM(1) TO IFORM(ISPEAR) CONTAIN IN CODED FORM DY(J)/DT FOR
C FORMATION PROCESSES.
C IEMOV(1) TO IEMOV(IARROW) CONTAIN IN CODED FORM DY(J)/DT FOR
C REMOVAL PROCESSES.
C NEQNS=NO. OF REACTIONS CONSIDERED,NEQNS L. T. 200
C LENGTH L.T. 500
C
C SEARCH TO FIND IF KTH EQN CONTAINS SPECIES J IN ROW I2
  IARROW=0
  ISPEAR=0
  DO 90 I2=1,6
  DO 90 K=1,NEQNS
    IF(IAC(I2,K)-J)90,5,90
C
C KTH EQN CONTAINS Y(J) IN ROW I2
  5 IF(I2-3)10,10,50
C
C KTH EQN IS REMOVAL EQN FOR Y(J), CALCULATE REMOVAL TERM IN IREMOVE
C STARTING AT IARROW
  10 IARROW=IARROW+1
    IF(IAC(8,K)-2)20,25,15
  15 IF(IAC(8,K)-4) 25,25,30
  20 IEMOV(IARROW)=-2
    GO TO 35
  25 IEMOV(IARROW)=-3
    GO TO 35
  30 IEMOV(IARROW)=-4
  35 IARROW=IARROW+1
    IEMOV(IARROW)=IAC(7,K)
    DO 45 II=1,3
      IF(IAC(II,K))95,45,40
  40 IARROW=IARROW+1
    IEMOV(IARROW)=IAC(II,K)
  45 CONTINUE
    GO TO 90
C
C KTH EQN IS FORMATION EQUATION FOR Y(J), CALCULATE FORMATION TERM IN
C IFORM, STARTING AT ISPEAR
  50 ISPEAR=ISPEAR+1
    IF(IAC(8,K)-2)60,65,55
  55 IF(IAC(8,K)-4)65,65,70
  60 IFORM(ISPEAR)=2
    GO TO 75
  65 IFORM(ISPEAR)=3
    GO TO 75
  70 IFORM(ISPEAR)=4
  75 ISPEAR=ISPEAR+1
    IFORM(ISPEAR)=IAC(7,K)
    DO 85 II=1,3
      IF(IAC(II,K))95,85,80
  80 ISPEAR=ISPEAR+1
    IFORM(ISPEAR)=IAC(II,K)
  85 CONTINUE
  90 CONTINUE
    GO TO 105
  95 WRITE(6,100)
  100 FORMAT(23H ERROR IN SUBROUTINE DY)
  105 RETURN
      END
DY000000
DY500005
DY500010
DY500015
DY500020
DY500025
DY500030
DY500035
DY500040
DY500045
DY500050
DY500055
DY500060
DY500065
DY500070
DY500075
DY500080
DY500085
DY500090
DY500095
DY500100
DY500105
DY500110
DY500115
DY500120
DY500125
DY500130
DY500135
DY500140
DY500145
DY500150
DY500155
DY500160
DY500165
DY500170
DY500175
DY500180
DY500185
DY500190
DY500195
DY500200
DY500205
DY500210
DY500215
DY500220
DY500225
DY500230
DY500235
DY500240
DY500245
DY500250
DY500255
DY500260
DY500265
DY500270
DY500275
DY500280
DY500285
DY500290
DY500295
DY500300
DY500305

```

B8

```
*IBFTC DIFFER LIST
SUBROUTINE DIFFER(INPUT,INSTOP,LDEN,IPART,LENGTH,LFLAG,ICOR,LICOR)
DIMENSION INPUT(500),IPART(500),ICOR(500)
C
C SUBROUTINE TAKES PORTION OF CORE FROM INPUT(I) TO ANS INCLUDING
C INPUT(INSTOP) AND CALCULATES PARTIAL DERIVATIVE OF IT W.R.T. Y(LDEN)
C INSTOP L.T. 200
C LDEN=5,6,...,NSPECI+4
C DERIVATIVE IS STORED IN IPART(I) TO IPART(LENGTH)
C IF LENGTH = 0 , DERIVATIVE IS ZERO
  IARROW=0
  IPOINT=0
  INDEX=1
C
C CHECK FOR END OF INPUT PORTION
  5 IF(INPUT(INDEX))10,75,10
  10 IF(IABS(INPUT(INDEX))-4)15,15,80
  15 IF(IABS(INPUT(INDEX))-1)70,70,20
C
C SCAN SERIES FOR LDEN
  20 INSTOP=IABS(INPUT(INDEX))
  ICOUNT=0
  DO 30 I=2,INSTOP
    II=INDEX+I
    IF(INPUT(II)-LDEN)30,25,30
  25 ICOUNT=ICOUNT+1
  30 CONTINUE
  IF(ICOUNT-1)35,40,40
C
C NO LDEN IN SERIES
  35 GO TO 70
C
C ONE LDEN IN SERIES,CALCULATE PARTIAL IN IPART,STARTING AT IARROW
  40 IARROW=IARROW+1
  IPART(IARROW)=IABS(INPUT(INDEX))-1
  IPART(IARROW)=ISIGN(IPART(IARROW),INPUT(INDEX))
  IPART(IARROW+1)=INPUT(INDEX+1)
  IARROW=IARROW+1
  45 DO 55 I=2,INSTOP
    II=INDEX+I
    IF(INPUT(II)-LDEN)50,55,50
  50 IARROW=IARROW+1
  IPART(IARROW)=INPUT(II)
  55 CONTINUE
  IF(ICOUNT-1)60,70,60
C
C LDEN OCCURS MORE THAN ONCE IN SERIES,DIFFERENTIATE AGAIN
  60 DO 65 LL=2,ICOUNT
    IARROW=IARROW+1
  65 IPART(IARROW)=LDEN
C
C RESET INDEX
  70 INDEX=INDEX+IABS(INPUT(INDEX))+1
  IF(INDEX-INSTOP) 5,5,75
  75 LENGTH=IARROW
  LICOR=IPOINT
  GO TO 90
  80 WRITE(6,85)
  85 FORMAT(27H ERROR IN SUBROUTINE DIFFER)
  90 RETURN
  END
```

DIFR0000  
DIFR0005  
DIFR0010  
DIFR0015  
DIFR0020  
DIFR0025  
DIFR0030  
DIFR0035  
DIFR0040  
DIFR0045  
DIFR0050  
DIFR0055  
DIFR0060  
DIFR0065  
DIFR0070  
DIFR0075  
DIFR0080  
DIFR0085  
DIFR0090  
DIFR0095  
DIFR0100  
DIFR0105  
DIFR0110  
DIFR0115  
DIFR0120  
DIFR0125  
DIFR0130  
DIFR0135  
DIFR0140  
DIFR0145  
DIFR0150  
DIFR0155  
DIFR0160  
DIFR0165  
DIFR0170  
DIFR0175  
DIFR0180  
DIFR0185  
DIFR0190  
DIFR0195  
DIFR0200  
DIFR0205  
DIFR0210  
DIFR0215  
DIFR0220  
DIFR0225  
DIFR0230  
DIFR0235  
DIFR0240  
DIFR0245  
DIFR0250  
DIFR0255  
DIFR0260  
DIFR0265  
DIFR0270  
DIFR0275  
DIFR0280  
DIFR0285  
DIFR0290  
DIFR0295  
DIFR0300

\$IBFTC REFACT LIST	REFA0000
SUBROUTINE REFACT(INPUT0,NSPECI,INPUT,LENGTH,JK)	REFA0005
DIMENSION INPUT0(500),INPUT(500),IWORK(500),ISTICK(500),INPUTY(500)	REFA0010
1)	REFA0015
C	REFA0020
C SUBROUTINE COMPLETELY FACTORS INPUT(0:1) TO INPUT0(LENGTH) AND RETURN	REFA0025
C RESULT IN INPUT(1) TO INPUT(LENGTH). LENGTH IS CHANGED IN ROUTINE	REFA0030
C LENGTH 6. T. OR E. 1000	REFA0035
DO 5 I=1,LENGTH	REFA0040
5 INPUT(I)=INPUT0(I)	REFA0045
IBLOCK=0	REFA0050
IQUIT=1	REFA0055
10 DO 15 I=1,IQUIT	REFA0060
15 ISTICK(I)=0	REFA0065
IBEGIN=IBLOCK+1	REFA0070
C	REFA0075
C SEARCH INPUT AREA UNTIL FIND FIRST PAIR OF CLOSED PARENTHESES TO	REFA0080
C RIGHT OF IBLOCK	REFA0085
IF( (IBLOCK-LENGTH+6)20,20,175	REFA0090
20 DO 40 INDEX=IBEGIN,LENGTH	REFA0095
IF( (ABS(INPUT(INDEX))-1000)40,40,25	REFA0100
25 IF( (INPUT(INDEX))30,35,35	REFA0105
30 MARK=INDEX	REFA0110
GO TO 45	REFA0115
35 LMARK=INDEX	REFA0120
40 CONTINUE	REFA0125
45 ASSIGN 10 TO LSWTCH	REFA0130
C	REFA0135
C NOW LH PARENTHESIS IS AT LMARK AND RH PARENTHESIS IS AT MARK, PICK	REFA0140
C OFF EVERYTHING IN BETWEEN	REFA0145
ISTART=LMARK +1	REFA0150
ISTOP=MARK-1	REFA0155
IF( (ISTOP-ISTART-6)110,50,50	REFA0160
50 II=0	REFA0165
DO 55 I=ISTART,ISTOP	REFA0170
II=II+1	REFA0175
55 ISTICK(II)=INPUT(I)	REFA0180
IQUIT=II	REFA0185
C	REFA0190
C FACTOR EVERYTHING BETWEEN LMARK AND MARK	REFA0195
CALL FACTOR(ISTICK,IQUIT,NSPECI,IWORK,LMAX,ISPRED)	REFA0200
IF(LMAX) 60,110,60	REFA0205
C	REFA0210
C PUT FACTORED VERSION (IWORK) INTO INPUT BETWEEN LMARK AND MARK	REFA0215
60 IHAVE =MARK-LMARK-1	REFA0220
IF( (ISPRED - IHAVE)65,100,85	REFA0225
C	REFA0230
C TOO MUCH ROOM BETWEEN LMARK AND MARK, COLLAPSE SOME	REFA0235
65 IMOVE=IHAVE-ISPRED	REFA0240
II=MARK-IMOVE	REFA0245
INPUT(II)=INPUT(MARK)	REFA0250
INPUT(MARK)=0	REFA0255
ISTOP=LENGTH-MARK	REFA0260
IF( (ISTOP)165,80,70	REFA0265
70 DO 75 I=1,ISTOP	REFA0270
JJ=II+I	REFA0275
I2=MARK+I	REFA0280
INPUT(JJ)=INPUT(I2)	REFA0285
75 INPUT(I2)=0	REFA0290

B10

```
      80 LENGTH=LENGTH-IMOVE
      GO TO 100
C
C NEED MORE ROOM,MOVE EVERYTHING TO RIGHT OF AND INCLUDING MARK TO
C RIGHT ONE SPACE
      85 ISTOP=LENGTH-MARK+1
      90 DO 95 I=1,ISTOP
          II=LENGTH+1-I
          95 INPUT(II+1)=INPUT(II)
          LENGTH=LENGTH+1
          IHAVE=IHAVE+1
          IF(ISPRED-IHAVE) 100,100,90
C
C DONT HAVE TO MOVE THINGS AROUND
      100 DO 105 I=1,ISPRED
          II=LMARK+I
          105 INPUT(II)=IWORK(I)
          GO TO 10
C
C NEW SEARCH FOR )
      110 DO 115 I=1,IQUIT
          115 ISTICK(I)=0
          IBLOCK=MARK
          LMARK=MARK
          120 IBEGIN = IBLOCK+1
          DO 130 INDEX=IBEGIN,LENGTH
              IF(ABS(INPUT(INDEX))-1000)130,130,125
          125 IF(INPUT(INDEX))135,175,175
          130 CONTINUE
          GO TO 175
          135 MARK=INDEX
C
C NOW ) IS AT LMARK AND ) IS AT MARK,PICK OFF EVERYTHING IN BETWEEN
          IF(MARK-LMARK-6)140,140,145
          140 LMARK=MARK
          IBLOCK=MARK
          GO TO 120
C
C NOT ENOUGH ROOM TO FACTOR
      145 ISTART=LMARK+1
          ISTOP=MARK-1
          II=0
          DO 150 I=ISTART,ISTOP
              II=II+1
          150 ISTICK(II)=INPUT(I)
          IQUIT=II
          CALL FACTGR(ISTICK,IQUIT,NSPECI,IWORK,LMAX,ISPRED)
          IF(LMAX) 160,155,160
C
C CANT FACTOR ) GO BACK AND SEARCH FOR NEXT )
      155 IBLOCK=MARK
          LMARK=MARK
          GO TO 110
C
C PUT FACTORED PART IN INPUT BETWEEN LMARK AND MARK
      160 GO TO 60
      165 WRITE(6,170)
      170 FORMAT(27H ERROR IN SUBROUTINE REFACT)
      175 RETURN
          END
      REFA0295
      REFA0300
      REFA0305
      REFA0310
      REFA0315
      REFA0320
      REFA0325
      REFA0330
      REFA0335
      REFA0340
      REFA0345
      REFA0350
      REFA0355
      REFA0360
      REFA0365
      REFA0370
      REFA0375
      REFA0380
      REFA0385
      REFA0390
      REFA0395
      REFA0400
      REFA0405
      REFA0410
      REFA0415
      REFA0420
      REFA0425
      REFA0430
      REFA0435
      REFA0440
      REFA0445
      REFA0450
      REFA0455
      REFA0460
      REFA0465
      REFA0470
      REFA0475
      REFA0480
      REFA0485
      REFA0490
      REFA0495
      REFA0500
      REFA0505
      REFA0510
      REFA0515
      REFA0520
      REFA0525
      REFA0530
      REFA0535
      REFA0540
      REFA0545
      REFA0550
      REFA0555
      REFA0560
      REFA0565
      REFA0570
      REFA0575
      REFA0580
      REFA0585
      REFA0590
```

```

$IBFTC FACTOR LIST
SUBROUTINE FACTOR(INPUT,LENGTH,NSPECI,IFACT,LMAX,ISPRED)
DIMENSION INPUT(500),IFACT(500),ICHECK(500),IMESS(500)
C
C SUBROUTINE FACTORS OUT LMAX, THE SPECIE OCCURRING MOST OFTEN, FROM
C INPUT(1) TO INPUT(LENGTH). FACTORED VERSION IS RETURNED IN IFACT(1)
C TO IFACT(ISPRED).
C NSPECI=NO. OF SPECIES
C LENGTH L.T. 500
C NSPECI L.T. 100
  I5=NSPECI+4
  DO 5 I=5,15
    5 ICHECK(I)=0
    LCOUNT=0
C
C COUNT HOW MANY TIMES EACH SPECIES IS USED
  INDEX=1
  10 IF(INPUT(INDEX)) 15,70,15
C
C IF HIT ZERO GET OUT
  15 IF(IABS(INPUT(INDEX))-4) 20,20,185
  20 IF(IABS(INPUT(INDEX))-2) 40,40,25
  25 ISTOP=IABS(INPUT(INDEX))
C
C CHECK FOR REPEATED SPECIES IN TERM
  DO 35 I=2,ISTOP
    II=INDEX+I
    DO 35 J=2,ISTOP
      JJ=INDEX+J
      IF(I-J) 30,35,30
  30 IF(INPUT(II)-INPUT(JJ)) 35,60,35
  35 CONTINUE
  GO TO 50
C
C NO REPEATED SPECIES IN TERM
  40 IF(IABS(INPUT(INDEX))-1) 185,65,45
  45 I=INPUT(INDEX+2)
  ICHECK(I)=ICHECK(I)+1
  GO TO 65
  50 DO 55 I=2,ISTOP
    JJ=INDEX+I
    II=INPUT(JJ)
    55 ICHECK(II)=ICHECK(II)+1
    GO TO 65
C
C REPEATED SPECIES IS II FROM STATEMENT 4
  60 II=INPUT(JJ)
  ICHECK(II)=ICHECK(II)-1
  GO TO 50
C
C RESET INDEX TO HIT NEXT TERM
  65 INDEX=INDEX+ IABS(INPUT(INDEX))+1
  IF(INDEX-LENGTH) 10,10,70
  70 LENGTH=INDEX-1
C
C NOW THE ICHECK(L) CONTAINS THE NUMBER OF TIMES THE SPECIES L OCCURS
C IN LOCATIONS INPUT(1) TO INPUT(LENGTH)
C
C SCAN THE ICHECK TO SEE IF FACTORABLE.

```

```

FACT0000
FACT0005
FACT0010
FACT0015
FACT0020
FACT0025
FACT0030
FACT0035
FACT0040
FACT0045
FACT0050
FACT0055
FACT0060
FACT0065
FACT0070
FACT0075
FACT0080
FACT0085
FACT0090
FACT0095
FACT0100
FACT0105
FACT0110
FACT0115
FACT0120
FACT0125
FACT0130
FACT0135
FACT0140
FACT0145
FACT0150
FACT0155
FACT0160
FACT0165
FACT0170
FACT0175
FACT0180
FACT0185
FACT0190
FACT0195
FACT0200
FACT0205
FACT0210
FACT0215
FACT0220
FACT0225
FACT0230
FACT0235
FACT0240
FACT0245
FACT0250
FACT0255
FACT0260
FACT0265
FACT0270
FACT0275
FACT0280
FACT0285
FACT0290

```

B12

```
  NSTOP=NSPEC I*4
  DO 75 I=5,NSTOP
  IF(ICHECK(I)-2175,80,80)
75 CONTINUE
```

```
CANNOT BE FACTORED
  LMAX=0
  GO TO 195
```

```
SCAN THE ICHECK TO FIND LMAX, THE SPECIE OCCURRING MOST OFTEN
80 DO 90 I=5,NSTOP
  IF(ICHECK(I)-LCOUNT)90,90,85
85 LMAX=I
  LCOUNT=ICHECK(I)
90 CONTINUE
```

```
FACTOR AND ARRANGE PARENTHESIS
```

```
  IFACT(1)=LMAX
  IFACT(2)=1001
  IARROW=1
  ISPEAR=3
  INDEX=1
95 IF(INPUT(INDEX)) 100,175,100
100 IF((ABS(INPUT(INDEX))-4)105,105,185
105 IF((ABS(INPUT(INDEX))-1)185,120,110
110 ISTOP=ABS(INPUT(INDEX))
  DO 115 I=2,ISTOP
  II=INDEX+I
  IF(INPUT(II)-LMAX)115,135,115
115 CONTINUE
  GO TO 125
120 ISTOP=1
```

```
NO LMAX IN THIS SERIES OF SPECIES,SHIP SERIES TO IMESS
```

```
125 IMESS(IARROW)=INPUT(INDEX)
  DO 130 I=1,ISTOP
  IARROW=IARROW+1
  II=INDEX+I
130 IMESS(IARROW)=INPUT(II)
  IARROW=IARROW+1
  GO TO 170
```

```
LMAX IS IN THIS SERIES, COLLAPSE SERIES INTO IFACT
```

```
135 IDUM=ABS(INPUT(INDEX))-1
  IFACT(ISPEAR)=ISIGN(IDUM,INPUT(INDEX))
  ISPEAR=ISPEAR+1
140 IFACT(ISPEAR)=INPUT(INDEX+1)
  IDROP=0
  DO 165 I=2,ISTOP
  II=INDEX+I
  IF(IDROP)150,145,150
145 IF(INPUT(II)-LMAX)150,160,150
150 ISPEAR=ISPEAR+1
155 IFACT(ISPEAR)=INPUT(II)
  GO TO 165
160 IDROP=1
165 CONTINUE
  ISPEAR=ISPEAR+1
```

FACT0295  
FACT0300  
FACT0305  
FACT0310  
FACT0315  
FACT0320  
FACT0325  
FACT0330  
FACT0335  
FACT0340  
FACT0345  
FACT0350  
FACT0355  
FACT0360  
FACT0365  
FACT0370  
FACT0375  
FACT0380  
FACT0385  
FACT0390  
FACT0395  
FACT0400  
FACT0405  
FACT0410  
FACT0415  
FACT0420  
FACT0425  
FACT0430  
FACT0435  
FACT0440  
FACT0445  
FACT0450  
FACT0455  
FACT0460  
FACT0465  
FACT0470  
FACT0475  
FACT0480  
FACT0485  
FACT0490  
FACT0495  
FACT0500  
FACT0505  
FACT0510  
FACT0515  
FACT0520  
FACT0525  
FACT0530  
FACT0535  
FACT0540  
FACT0545  
FACT0550  
FACT0555  
FACT0560  
FACT0565  
FACT0570  
FACT0575  
FACT0580  
FACT0585

C RESET INDEX	FACT0590
170 INDEX=INDEX+IABS(INPUT(INDEX))+1	FACT0595
IF(INDEX=LENGTH) 95,95,175	FACT0600
C	FACT0605
C SET RIGHT PARENTHESIS	FACT0610
175 IFACT(ISPEAR)=-1001	FACT0615
C	FACT0620
C NOW SWAP IMESS ON REAR OF IFACT STARTING AT ISPEAR	FACT0625
IARROW=IARROW-1	FACT0630
DO 180 I=1,IARROW	FACT0635
II=ISPEAR+I	FACT0640
180 IFACT(II)=IMESS(I)	FACT0645
ISPREO=ISPEAR+IARROW	FACT0650
GO TO 195	FACT0655
185 WRITE(6,190)	FACT0660
190 FORMAT(27H ERROR IN SUBROUTINE FACTOR)	FACT0665
195 RETURN	FACT0670
END	FACT0675

Subroutine OUT takes the highly factored version of the removal or formation reactions as required and prepares the hollerith output characters for each term of the factored equation. The species are coded as Y(X) and the rate constants as C(Z). Each term of the series is identified by a factorizing parenthesis as a species or a rate constant. Into the first word of the OUTPUT region is stored an equal sign. Whenever a factorizing parenthesis is found, be it open or closed, the BCD character for the open or closed parenthesis is stored in the next word of the OUTPUT region. The actual insertion of the BCD equivalent of the binary term is inserted between the parentheses of Y and C by subroutine CODER. This latter subroutine also inserts the BCD characters for addition (+) and for multiplication (\*) into OUTPUT words as required.

Upon exit from OUT, the FORM or REMV terms preceded by or followed by proper BCD arithmetic symbols are located in the OUTPUT region. Each word of this region contains one BCD coded quantity. It can be either a species Y, a rate constant C, an open or closed parenthesis, or a plus sign. The following statements, beginning on page B14, are a listing of the FORTRAN statements for subroutine OUT.

Subroutine CODER is called by OUT and sets up the BCD character for the information fed to it by OUT. OUT calls this subroutine if the word to be coded is a species or a rate constant, tells the subroutine if it is a species or a rate constant and whether the species should have an asterisk preceding it or following it in the FORTRAN code. Upon return to OUT this BCD coded word is stored in the next word of the OUTPUT region.

The following statements, beginning on page B15, are a listing of the MAP code and can be used on an IBM-7044 as well as on an IBM-7094.



IB 14

```

SUBROUTINE LIST
COMMON (OUT, IN, LENGTH, JARRAY)
DIMENSION IN(100), ISCO(100)
DATA (0, 66, 80), (, 66, 80), (, 66, 80), (, 66, 80), (, 66, 80), (, 66, 80)
11 //
12 JARRAY=1
13 OUTPUT(1)=0
14 LENGTH=LENGTH-20 GO TO 880
15 IN=1
65 JARRAY=JARRAY+1
16 I=ABS(IN-INDEX)-1 GO TO 225 225 225 110
170 I=IN-INDEX+1 ISCO(1)=0 220
180 OUTPUT(JARRAY)=0
190 GO TO 770
220 OUTPUT(JARRAY)=0
230 GO TO 770
235 I=ABS(IN-INDEX)-1 4 130 210 655
240 I=GO TO-INDEX+INDEX+1
250 OUTPUT(JARRAY)=0
260 JARRAY=JARRAY+1
270 MASK=0
280 JJJ=1
290 CALL COVER (I, GO TO, MASK, JJJ)
300 OUTPUT(JARRAY)=MASK
310 I=ABS(IN-INDEX)-1 11 665 660 645
340 IN=INDEX+INDEX+1
350 GO TO 770
365 I=STOP I=ABS(IN-INDEX)
370 GO 550 I=2 I=STOP
380 JARRAY=JARRAY+1
390 I=INDEX+1
400 I=GO TO-INDEX+1 4
410 MASK=0
420 JJJ=2
430 CALL COVER (I, GO TO, MASK, JJJ)
440 OUTPUT(JARRAY)=MASK
550 CONTINUE
560 IN=INDEX+INDEX+ABS(IN-INDEX)
570 GO TO 770
585 I=IN-INDEX+1 60 685 645
590 OUTPUT(JARRAY)=0
600 JARRAY=JARRAY+1
615 I=GO TO-INDEX+1 4
620 MASK=0
630 JJJ=3
640 CALL COVER (I, GO TO, MASK, JJJ)
650 OUTPUT(JARRAY)=MASK
670 IN=INDEX+INDEX+1
680 I=INDEX-LENGTH 55 65 275
690 JARRAY=JARRAY+1
700 GO TO 595
850 JARRAY=1
860 GO TO 595
885 WRITE (6, 90)
900 FORMAT ('24H ERROR IN SUBROUTINE (OUT)')
95 RETURN
END

```

000005
000010
000015
000020
000030
000035
000040
000045
000050
000055
000060
000065
000070
000075
000080
000085
000090
000095
000100
000105
000110
000115
000120
000125
000130
000135
000140
000145
000150
000155
000160
000165
000170
000175
000180
000185
000190
000195
000200
000205
000210
000215
000220
000225
000230
000235
000240
000245
000250
000255
000260
000265
000270
000275
000280
000285
000290
000295
000300
000305
000310

```

SS EMMAP CCOBRR
CCOBR  SSAVE  11 22
        CCLA  33 44
        SSTA  CCOBBA
        CCLA  44 44
        SSTA  CCOBEB
        SSTA  CCOBED
        SSTA  CCOBEE
        SSTA  CCOBEE
        SSTA  CCOBEB
        SSTA  CCOBBB
        SSTA  CCOBB7
        SSTA  CCOBB4
        SSTA  CCOBES
        CCLA  55 44
        SSTA  CCOBEC
        SSTEZ  TTEMP
CCOBE0  CCLAL  ***
        AANA  MASK
CCOBE1  SSBH  ***
        CCLA  ***
        TESX  .COEVA 44
        LLGL  118
        LKXA  TTHRE 11
        CCLA  ZZERO
CCOBE1  LLGL  66
        ITNZ  ***2
        TTX  CCOE11111
        LLGR  118
        XKCA
CCOBE8  CWS  ***
        SSHA  TTEMP 1
        CCLA  FEUR
        SSB  TTEMP
        FPAX  CO 1
        CCLA  PPARAN
CCOBE2  TTX  ***21111
        TTRA  CCOBE3
        ABS  6
        ADD  BLANK
        TTRA  CCOBE2
CCOBE3  CQRS  ***
        CDEC  CCLA  ***
        FPAX  CO 1
        TTRA  ***4 1
        TTRA  CCOBE5
        TTRA  CCOBE4
CCOBE7  CCLA  ***
        TTRA  CCOBE6
CCOBE4  CDD  ***
        CCLA  MASK
        LLGR  6
        XKCA
        TTRA  CCOBE6
CCOBE5  CCLA  ***
        ADD  FEUR
CCOBE6  STU  ***
        RETURN CCOBR
ITHREE  CDT  CCCCCCCCCC03
ZZERO   CDT  CCCCCCCCCC00
FEUR    CDT  CCCCCCCCCC04
PPARAN  CDT  CCCCCCCCCC04
BLANK   CDT  CCCCCCCCCC04
MASK    CDT  CCCCCCCCCC04
TEMP    CDT  7777CCCC00
        BSS  11
        FENO

```

B16

Upon exit from subroutine OUT, all of the terms of the given series are BCD coded and stored in the OUTPUT region. Since each word of this region contains one coded species, one rate constant, one equal sign, one plus sign, or an open or closed parenthesis, each word will contain some imbedded blank characters. The purpose of subroutine DECOD is to scan the OUTPUT region and remove any blank characters it finds and to collapse the remaining valid characters.

On exit from DECODE the required BCD coded equation is sitting in the ID region devoid of all imbedded blank characters and is ready to be printed and punched.

The following statements, beginning on page B17, are a listing of the MAP code for this subroutine and is acceptable to either the IBM-7044 or IBM-7094 computer.

```

$IBMAP DECODE
DECODE SAYE 1,2
      CLA 4,4
      STA DECOD4
      CLA 5,4
      STA **1
      CLA **
      PAX 0,1
      ADD 3,4
      STA DECOD1
      CLA 6,4
      STA DECOD8
      CLA MASK
      STO DECOD2
      STZ COUNT
      LXA SIX,2
      LXA SIX,4
DECOD1 LDQ **1
      LGL 6
      CAS BLANK
      TRA **2
      TRA DECOD3
DECOD2 ALS 30
DECOD4 ORS **
      CLA DECOD2
      SUB SIX
      STO DECOD2
      TIX DECOD3,2,1
      CLA COUNT
      ADD ONE
      STO COUNT
      CLA DECOD4
      SUB ONE
      STO DECOD4
      CLA MASK
      STO DECOD2
      LXA SIX,2
DECOD3 CLA ZERO
      TIX DECOD1+1,4,1
      LXA SIX,4
      TIX DECOD1,1,1
      CLA DECOD2
      STO DECOD5
      CLA DECOD4
      STO DECOD6
DECOD7 CLA BLANK
DECOD5 ALS **
DECOD6 ORS **
      CLA DECOD5
      SUB SIX
      STO DECOD5
      TIX DECOD7,2,1
      CLA COUNT
      ADD ONE
DECOD8 STO **
      RETURN DECODE
MASK ALS 30
SIX DEC 6
ONE DEC 1
BLANK UCT 000CC000060
ZERO UCT 000CC00CC00C
COUNT BSS 1
      END

```

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13. ABSTRACT <p>With the availability of numerical techniques for solving an extensive set of nonlinear differential equations and high-speed computers for performing the calculations, interest in solving the unrestricted reaction-rate equations is growing among ionospheric researchers. In view of this, the author has continued to refine the techniques that he previously developed.</p> <p>The computer code, as discussed here, is written to solve the photochemical behavior of 15 atmospheric species; these species are electrons, <math>C</math>, <math>O_2</math>, <math>O_3</math>, <math>NO_2</math>, <math>O^+</math>, <math>O_2^+</math>, <math>N_2^+</math>, <math>NO^+</math>, <math>NO</math>, <math>N</math>, <math>NO_2</math>, <math>O_3</math>, <math>N_2O</math>, and <math>O</math>. Built into the code are 168 reactions that can conceivably take place among these constituents. Several examples of the results obtained using the code are presented, including the buildup of ionization from zero concentrations at altitudes in the D and E regions and the deionization of an atmosphere with high initial electron densities. The diurnal variation of the atmospheric constituents is also presented along with profiles for the above-mentioned species from 60 km to 120 km.</p> <p>The computer codes are included in their entirety with complete explanations on their usage.</p>		

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