

Daytime and Nighttime Photochemical Reactions of the Pure Oxygen System

by

Kwang Sik Yun*

National Center for Atmospheric Research Boulder, Colorado

(Received July, 3, 1969)

순수 산소계의 주간 및 야간 광화학반응

National Center for Atmospheric Research Boulder, Colorado

윤 광 식*

(1969. 7. 3 접수)

ABSTRACT

Studies of photochemical reactions of the pure oxygen atmosphere are made using reaction rate constants and atmospheric data available in the latest literature. The daytime and nighttime variations in atomic oxygen and ozone are computed, based on three different conditions: 1) photochemical equilibrium, 2) direct integrations of the rate equations with modifications and approximation to the equations, and 3) by numerical integrations. The departure from the photochemical equilibrium concentrations during day and nighttime are discussed by comparing the results obtained from the three conditions.

I. INTRODUCTION

Since the appearance of Chapman's paper(1930) on ozone and atomic oxygen in the upper atmosphere, of the work by Wulf and Deming (1936) in ozone photochemistry, and of the paper by Bates and Nicolet (1950) on the photochemistry of atmospheric water vapor numerous authors have made similar studies on other chemical species which pertain to atmospheric phenomena. Oxygen allotropes, nitrogen-oxygen compounds, and hydrogen-oxygen compounds have been studied more extensively than other species since these compounds are the major constituents of the atmosphere. Especially the oxygen allotropes have been a major

subject in studies of atmospheric chemistry. This is due partially to interest in the ozone layer and in atmospheric heating by the recombination of atomic oxygen into molecular oxygen and ozone. A survey of the many existing papers on the photochemistry of the oxygen allotropes shows that most investigators agree on the nature and mechanism of the photochemical reactions of the oxygen allotropic species. However, some results, such as the number densities of the allotropes and the relaxation time (or characteristic time), vary considerably among investigators, in some cases by an order of magnitude or more. This disagreement can be attributed to the adoption of different atmospheric models, the use of different values for the reaction rate constants, and different approximation or modification methods for the

* Present address: Department of Chemistry, The University of Mississippi, University, Mississippi.

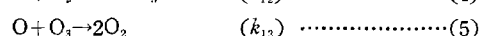
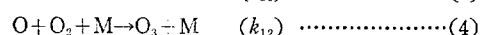
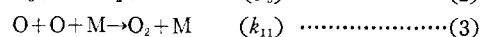
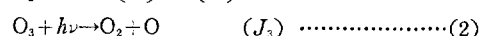
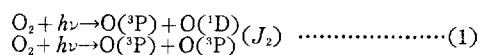
integration of the rate equations.

A thorough review and compilation of the kinetic rate data for the reactions of the neutral atmospheric species has recently been undertaken in this laboratory. The purpose of this paper is three-fold. First, it discusses the photochemical equilibrium behavior of the oxygen allotropes, using the latest available values of the rate constants; results are compared with other previous results. Second, it describes an investigation of the possible departure from the photochemical equilibrium behavior of the species, by the direct integration of the rate equations. Third, it describes attempts to obtain simultaneous solutions of the rate equations by numerical methods. The simultaneous solutions by the numerical method do not add much insight into physical or chemical mechanisms of the distribution and the time variation of the species. However, we should expect accurate values for the distribution and the time variation from the numerical integration of the equations.

The atmospheric model, the total number density, and the uniform mixing ratios of N_2 and O_2 are taken from the publication by CIRA (1965).

II. Photochemical Equilibrium Condition

There are many chemical processes involved with the oxygen allotropes which can undergo many chemical processes resulting from the excitation of atoms and molecules or thermal dissociation of molecules, but in this discussion we limit the process to the five most important reactions, namely



where J 's are the photodissociation rate constants, k 's the reaction rate constants, and M is the third body atom or molecule. The detailed description and the calculation of the J values are given in the works by Nicolet (1964), Craig (1965), and Nawrocki and Papa (1963). Many authors employ the constant values $1 \times 10^{-9} \sim 10^{-7}$ and $3.0 \sim 8.0 \times 10^{-3}$ for J_2 and J_3 , respectively, since there is considerable uncertainty

involved in the values of J when these are plotted against the altitude. The values of J_2 and J_3 adopted in this paper are based on Horiuchi's work (1961) for the region below 80 km; for the region above 80 km the J_2 values are extrapolated from the values at the lower region and the constant value of 3.8×10^{-3} for J_3 is employed. The vertical profile of J_2 and J_3 is shown in Fig. 1. Also indicated in Fig. 1 by the circles are the values of J_2 and J_3 obtained by Catchpole (1964). The effect on the distribution numbers of the species and on other physical properties due to the discrepancies or uncertainty in the J values will be discussed in Section V. The values of k are based on the data reported by Schofield (1967). In the case of three-body recombination reactions (Eqs. 3 and 4) the rate constants vary to some extent according to the nature or species of the third body, and thus the effectiveness of the recombination may be altered. In this work we take the number density of the third body as the sum of the number densities of molecular nitrogen and oxygen. Young and Epstein (1962) chose the number density of the third body as

$$n(M) = n(O_2) + 0.6n(N_2)$$

where $n(O_2)$ and $n(N_2)$ are the number densities of the molecular oxygen and nitrogen, respectively. Our calculation shows that when such a correction for the third body concentration is made our results for the atomic oxygen and ozone concentration are increased by only a factor of about 1.1~1.2. The values of k employed in this work are given as follows:

$$k_{11} = 5.0 \times 10^{-34} \times (T)^{1/2} \text{ (molecules}^{-2}, \text{cc}^2, \text{sec}^{-1})$$

$$k_{12} = 7.5 \times 10^{-35} \times \exp(890/RT) \text{ (molecules}^{-2}, \text{cc}^2, \text{sec}^{-1})$$

$$k_{13} = \frac{1}{3} \left[5.6 \times 10^{-11} \times \exp(-5700/RT) + 2.4 \times 10^{-11} \times (T/256)^{1/2} \times \exp(-3070/T) + 5.0 \times 10^{-11} \times \exp(-3020/T) \right] \text{ (molecules}^{-1}, \text{cc, sec}^{-1})$$

where T and R are the absolute temperature and the gas constant, 1.98717 (cal., deg.⁻¹, mole⁻¹).

The rate of change of the oxygen allotropes is governed by the equations:

$$\begin{aligned} \frac{dn(O)}{dt} &= 2J_2n(O_2) + J_3n(O_3) - 2k_{11}n(M)n^2(O) \\ &\quad - k_{12}n(M)n(O)n(O_2) - k_{13}n(O)n(O_3) \quad \dots\dots\dots(6) \\ \frac{dn(O_2)}{dt} &= -J_2n(O_2) + J_3n(O_3) + k_{11}n(M)n^2(O) \end{aligned}$$

$$-k_{12}n(M)n(O)n(O_2)+2k_{13}n(O)n(O_3) \cdots (7)$$

$$\frac{dn(O_3)}{dt} = -J_3n(O_3) + k_{12}n(M)n(O)n(O_2) - k_{13}n(O)n(O_3) \cdots (8)$$

where $n(\quad)$ indicates the number density of the species (number of particles, cc^{-1}). The photochemical equilibrium number densities of the atomic molecular oxygen and ozone are obtained by solving Eqs. (6), (7), and (8) for the condition.

The dissociation of molecular oxygen into atomic oxygen indicated in Eq. (1) depends on the actual ultraviolet solar spectrum in the regions of the Schumann-Runge bands around 1750 Å and of the Herzberg bands around 2500 Å (see for example, Nawrocki and Papa (1964), Watanabe (1958), and Nicolet (1964)). As pointed out by a number of investigators the frequency distribution of the solar spectrum in the ultraviolet region can be related to the black body temperature of the sun, and it turns out that the relaxation time (or characteristic time during which the concentration reduces to $1/e$ of the initial value or increases to e times the initial value) is about 3×10^3 sec at the black body temperature of 6000°K and 10^4 sec at 5500°K . Therefore we assume that the oxygen molecules maintain nearly photochemical equilibrium; the equilibrium number density of O_2 is simply obtained from the total number density of the atmosphere with the uniform mixing ratio of the molecular oxygen.

Let $n_e(O)$ and $n_e(O_3)$ be the photochemical equilibrium number densities of O and O_3 , respectively. Then from Eq. (8).

$$n_e(O_3) = \frac{k_{12}n(M)n(O_2)n_e(O)}{J_3 + k_{13}n_e(O)} \cdots (9)$$

The substitution of $n_e(O_3)$ into Eq. (6) at the photochemical equilibrium condition yields a cubic equation in $n_e(O)$ with three real roots, only one of which is positive. However, the computation of these roots is complicated; in this work instead of solving the cubic equation, $n_e(O)$ and $n_e(O_3)$ are computed by simultaneously solving Eqs. (6) and (8) using the Newton-Raphson method, which will be discussed later.

Bates and Nicolet (1950) derived the expression of $n_e(O)$ and $n_e(O_3)$ for different regions of the atmosphere. In their derivation some terms in Eqs. (6) and (8), whose orders of magnitude are very small, are eliminated; this modification gives an equation quadratic in $n_e(O)$ which is easily soluble. Their formulas are listed in Table 1. For the region above 70 km they took only the photodissociation of molecular oxygen and the three-body recombination of atomic oxygen into account, and they assumed the condition $J_2 \gg k_{13}n_e(O)$ for the region below 100 km. The results in $n_e(O)$ and $n_e(O_3)$ based on constant values for J_2 and J_3 differ considerably from those based on the variable values for J_2 and J_3 , and the position of the maximum peak of $n_e(O)$ varies with changes in J_2 and J_3 . In Fig. 2 the variations of $n_e(O)$ and $n_e(O_3)$ are plotted. In Fig. 3 the factors

$$\left[1 + \frac{k_{12}J_3n(O_2)}{k_{11}J_2}\right]^{-1/2} \quad \text{and} \quad \left[1 + \frac{k_{13}}{J_3}n_e(O)\right]^{-1}$$

are plotted for O and O_3 , respectively; the factors indicate the relation among the approximations adopted in deriving the formula listed in Table 1. Since the values of k_{11} and k_{12} differ by less than an order of magnitude, a crude estimation indicates that the $n_e(O)$ concentration around the 100 km level is increased

TABLE 1. Photochemical Equilibrium Number Density Formulas of O and O_3

Altitude	$n_e(O)$	$n_e(O_3)$
Above 100 km	$\left[\frac{J_2n(O_2)}{k_{11}n(M)}\right]^{1/2}$	$\frac{k_{12}n(M)n(O_2)}{J_3 + k_{13}n_e(O)}n_e(O)$
70-100 km	$\left[\frac{J_2n(O_2)}{k_{11}n(M)}\right]^{1/2}$	$\frac{k_{12}n(M)n(O_2)}{J_3}n_e(O)$
60-70 km	$\left[J_2n(O_2)/k_{11}n(M)\left\{1 + \frac{k_{12}k_{13}}{k_{11}J_3}n(O_2)\right\}\right]^{1/2}$	$\frac{k_{12}n(M)n(O_2)}{J_3}n_e(O)$
Below 60 km	$\left[\frac{J_2J_3}{k_{12}k_{13}n(M)}\right]^{1/2}$	$\left\{\frac{J_2k_{12}n(M)}{J_3k_{13}}\right\}^{1/2}n(O_2)$

by the factor of $1 + \frac{1}{2} \frac{k_{13}}{J_3} n(O_2)$ from that at the 60 km level and that the $n_e(O_3)$ concentration is decreased by the factor $1 - \frac{k_{13}}{J_3} n_e(O)$.

III. Departure from Photochemical Equilibrium Behavior

a) Daytime Variation. Some works (Nicolet, 1964, 1965; Penndorf, 1949) on the diurnal variation in atomic oxygen and ozone based their calculations on the argument that some terms in Eqs. (6) and (8) contribute far less than others to the variation; this assumption makes it possible to integrate Eqs. (6) and (8) directly. Extensive calculations and integration of the rate equations in more generalized form have, however, been made recently by Wallace (1962), Leovy (1964), Hunt (1965), and Barth (1961) for nighttime variation. According to Wallace, the actual daytime atomic oxygen concentration may be ten times less than the equilibrium value in the region extending from below 60 km to about 85 km. He obtained the daytime atomic oxygen concentration by integrating Eq. (6), substituting the equilibrium formula, Eq. (9) for $n(O_3)$.

His formula is

$$n(O) = \left[\frac{J_2 n(O_2)}{k_{11} n(M) \left\{ 1 + \frac{k_{12} k_{13}}{k_{11} J_3} n(O_2) \right\}} \right]^{1/2} \left(\frac{Re^{2Q} - 1}{Re^{2Q} + 1} \right) \dots \dots \dots (10)$$

where

$$R = \frac{2J_2 n(O_2) + Q n_i(O)}{2J_2 n(O_2) - Q n_i(O)} \dots \dots \dots (11)$$

$$Q = \left[4J_2 k_{11} n(M) n(O_2) \left\{ 1 + \frac{k_{12} k_{13}}{k_{11} J_3} n(O_2) \right\} \right]^{1/2} \quad (12)$$

and $n_i(O)$ is the initial value of $n(O)$.

If the relation $Re^{2Q} \gg 1$ holds in Eq. (10), the formula of $n(O)$ reduces to the photochemical equilibrium expression of $n(O)$ listed in Table 1. Such a relation is attained if t approaches infinity or Q takes a value such that the R values become large.

The values of R , however, are very sensitive to the number of significant figures in the terms $2J_2 n(O_2)$ and $Q n_i(O)$, whose difference comprises the denominator of R . Because of much uncertainty involved in the rate constants it is not easy to obtain a precise value for R . The departure from the photochemical equilibrium concentration should depend

on the qualitative interpretation of values of Q , which is inversely proportional to the characteristic time.

In this section we perform calculations similar to those made by Wallace, extending the region from 40 km to 110 km. Also the approach adopted here is somewhat similar to Nicolet's (1964, 1965).

In order that Eqs. (6) and (8) be directly integrable some approximation or modification of these equation is necessary; such approximation is made by comparing the orders of magnitude of the terms in the equations with the values for $n(O)$ and $n(O_3)$, substituted by their equilibrium values. The values of the five terms contained in Eqs. (6) and (8) are plotted in Fig. 4.

Below 60 km we can neglect the term $2k_{11} n(O) n^2(O)$. Then Eq. (6) is modified to

$$\frac{dn(O)}{dt} = 2J_2 n(O_2) + J_3 n_e(O_3) - k_{12} n(M) n(O) n(O_2) - k_{13} n(O) n_e(O_3) \dots \dots \dots (13)$$

The solution to this equation is

$$n(O) = n_i(O) \exp \{ - [k_{12} n(M) n(O_2) + k_{13} n_e(O_3)] t \} + \frac{2J_2 n(O_2) + J_3 n_e(O_3)}{k_{12} n(M) n(O_2) + k_{13} n_e(O_3)} [1 - \exp \{ - [k_{12} n(M) n(O_2) + k_{13} n_e(O_3)] t \}] \dots \dots \dots (14)$$

where $n_e(O_3)$ is the equilibrium ozone concentration. The characteristic time of the atomic oxygen in this region is represented by

$$\tau = [k_{12} n(M) n(O_2) + k_{13} n_e(O_3)]^{-1} \dots \dots \dots (15)$$

In Eq. (15) the value of the second term is about two orders of magnitude less than that of the first one, and thus the characteristic time is approximated to

$$\tau = [k_{12} n(M) n(O_2)]^{-1} \dots \dots \dots (15a)$$

This indicates that the variation in atomic oxygen is mainly due to the recombination of atomic and molecular oxygen into ozone. A different approach to this case could be made. If we assume that the ozone concentration expressed by Eq. (9) is still valid at lower altitudes and that $J_3 > k_{13} n_e(O)$ holds, the second and third terms on the right-hand side of Eq. (13) cancel each other. The solution to the equation is different from Eq. (14) and is written as

$$n(O) = \left\{ \frac{2J_2 J_3}{k_{12} k_{13} n(M)} \right\}^{1/2} \left\{ \frac{Re^{2Q} - 1}{Re^{2Q} + 1} \right\} \dots \dots \dots (10a)$$

where

$$Q_a = \left[\frac{2J_2 k_{12} k_{13} n(M)}{J_3} \right]^{1/2} n(O_2) \dots\dots\dots (12a)$$

and R has a formula identical to Eq. (11), except that Q has been replaced by Q_a .

Eqs. (10a) and (12a) can be derived directly from the solution of the more generalized case, Eqs. (10b) and (12b), when the following condition, which is valid at lower altitudes, is applied to Eq. (10b).

$$\frac{k_{12} k_{13}}{k_{11} J_3} n(O_2) \gg 1$$

The characteristic time for the change in $n(O)$ expressed by Eq. (10a) is $(2Q_a)^{-1}$ and this quantity is roughly two orders larger than the value of C in Eq. (15a). The discrepancy is due to the fact that the contribution from the term $k_{12} n(O) n(O_2)$ to the variation in atomic oxygen is considered quite effective in Eq. (10a) but is ignored in Eq. (15a). This is an example which indicates that a rate equation can yield two entirely different solutions depending on how an approximation to the equation is made. Above the 60 km to 80 km region all the terms have about the same order of magnitude and therefore no terms can be eliminated from Eq. (6). Therefore Wallace's formula is the preferable solution for the concentration of atomic oxygen at these altitudes. Above 80 km to 90 km the term $k_{12} n(O) n(O_2)$ can be dropped from the rate equation, Eq. (6), and this results in a solution slightly different from the Wallace expression. The atomic oxygen concentration formula is now

$$n(O) = \left[\frac{J_2 n(O_2)}{k_{11} n(M) \left\{ 1 + \frac{1}{2} \frac{k_{12} k_{13}}{k_{11} J_3} n(O_2) \right\}} \right]^{1/2} \left(\frac{Re^{2Q_a} - 1}{Re^{2Q_a} + 1} \right) \dots\dots\dots (10b)$$

and

$$Q_b = \left[4J_2 k_{11} n(M) n(O_2) \left\{ 1 + \frac{k_{12} k_{13}}{2k_{11} J_3} n(O_2) \right\} \right]^{1/2} \dots\dots\dots (12b)$$

R has a formula identical with that in Eq. (11), except that Q has been replaced by Q_b . Q and Q_b have values of equal magnitude above 70 km, and below 60 km they differ by the factor of 2. Above 90 km the rate equation for atomic oxygen is greatly simplified since the $J_3 n(O_3)$ can be neglected. Thus the rate equation is expressed by

$$\frac{dn(O)}{dt} = 2J_2 n(O_2) - 2k_{11} n(M) n^2(O) \dots\dots\dots (16)$$

The solution to this equation is

$$n(O) = \left\{ \frac{J_2 n(O_2)}{k_{11} n(M)} \right\}^{1/2} \left(\frac{Re^{2Q_c} - 1}{Re^{2Q_c} + 1} \right) \dots\dots\dots (10c)$$

where

$$Q_c = 2[k_{11} J_2 n(M) n(O_2)]^{1/2} \dots\dots\dots (12c)$$

The formulas expressed by Eqs. (10c) and (12c) can also be derived from the corresponding formulas of Eqs. (10) and (12) when the condition

$$\frac{k_{12} k_{13}}{k_{11} J_3} n(O_2) \ll 1$$

is assumed valid in this region. Such a condition was also discussed in connection with the derivation of the photochemical equilibrium formulas, and the variation of $\frac{k_{12} k_{13}}{k_{11} J_3} n(O_2)$ against the altitude is shown in Fig. 3.

The characteristic time of the process expressed by Eq. (16) is

$$T = \frac{1}{2Q_c} = \frac{1}{4} \left\{ k_{11} J_2 n(M) n(O_2) \right\}^{-1/2} \dots\dots\dots (17)$$

and this formula differs slightly from that obtained by Nicolet (1965), his coefficient being 0.275, instead of 1/4.

The nonequilibrium behavior of ozone can be investigated by steps similar to those employed for atomic oxygen. However, unlike the case of atomic oxygen, the ozone rate equation allows no simple substitution for the atomic oxygen concentration in order to make the integration of the equation more tractable. Nicolet (1965), neglecting the three-body recombination reaction of atomic oxygen in Eq. (6), obtains the expression for the equilibrium atomic oxygen concentration

$$n_e(O) = \frac{2J_2 n(O_2) + J_3 n(O_3)}{k_{12} n(M) n(O_2) + k_{13} n(O_3)} \dots\dots\dots (18)$$

The substitution of $n_e(O)$ in Eq. (8) and the use of the relation $k_{13} n(O_3) \ll k_{12} n(M) n(O_2)$ yield two rate equations from Eq. (8).

$$\frac{dn(O_3)}{dt} = 2J_2 n(O_2) \dots\dots\dots (19a)$$

and

$$\frac{dn(O_3)}{dt} + \frac{2k_{13} J_3}{k_{12} n(M) n(O_2)} n^2(O_3) = 2J_2 n(O_2) \dots\dots\dots (19b)$$

The solutions to these equations are respectively

$$n(\text{O}_3) = n_i(\text{O}_3) \left[1 + \frac{2J_2 n(\text{O}_2)}{n_i(\text{O}_3)} t \right] \dots\dots\dots (20a)$$

and

$$n(\text{O}_3) = n(\text{O}_2) \left[\frac{k_{12} J_2 n(\text{M})}{k_{13} J_3} \right]^{1/2} \left(\frac{F e^{2\alpha t} - 1}{F e^{2\alpha t} + 1} \right) \quad (20b)$$

where

$$F = \frac{2J_2 n(\text{O}_2) + \alpha n_i(\text{O}_3)}{2J_2 n(\text{O}_2) - \alpha n_i(\text{O}_3)} \dots\dots\dots (21)$$

$$\alpha = 2 \left[\frac{k_{13} J_2 J_3}{k_{12} n(\text{M})} \right]^{1/2} \dots\dots\dots (22)$$

and $n_i(\text{O}_3)$ is the initial value of $n(\text{O}_3)$.

In Eq. (20a) the term $\frac{2J_2 n(\text{O}_2)}{n_i(\text{O}_3)}$ is quite small, i.e. the order of magnitude is roughly 10^{-4} in the region between 30 km to 90 km. Therefore about 10 % deviation in the concentration from the $n_i(\text{O}_3)$ value takes place during 10^3 seconds. The characteristic time of the ozone variation for the second case, Eq. (19b), is

$$\tau = \frac{1}{2\alpha} = \frac{1}{4} \left[\frac{k_{12} n(\text{M})}{k_{13} J_2 J_3} \right]^{1/2} \dots\dots\dots (23)$$

This formula is in agreement with Nicolte's expression except that we obtain the factor of $\frac{1}{4}$ instead of his factor 0.275.

In the derivation of Eqs. (20a) and (20b) we assumed that the condition $k_{13} n(\text{O}_3) \ll k_{12} n(\text{M}) n(\text{O}_2)$ is valid throughout the region above 40 km. As shown in Fig. 4, the term $k_{13} n(\text{O}) n(\text{O}_3)$ is about two orders of magnitude less than the terms $k_{12} n(\text{M}) n(\text{O}) n(\text{O}_2)$ and $J_3 n(\text{O}_3)$ which are the same in their values, but in the rate equation, Eq. (8), They have the opposite signs. From this fact we can consider that the terms $k_{12} n(\text{M}) n(\text{O}) n(\text{O}_3)$ and $J_3 n(\text{O}_3)$ cancel each other and the minor term $k_{13} n(\text{O}) n(\text{O}_3)$ contributes effectively to the rate process of ozone; thus Eq. (8) is modified to

$$\frac{dn(\text{O}_3)}{dt} = -k_{13} n(\text{O}) n(\text{O}_3) \dots\dots\dots (24)$$

With the substitution of the equilibrium formula

$$\left\{ \frac{J_2 J_3}{k_{12} k_{13} n(\text{M})} \right\}^{1/2}$$

for $n(\text{O})$ the solution of Eq. (24) is obtained.

$$n(\text{O}_3) = n_i(\text{O}_3) e^{-\alpha t} \dots\dots\dots (25)$$

where

$$\alpha = \left[\frac{k_{13} J_2 J_3}{k_{12} n(\text{M})} \right]^{1/2} \dots\dots\dots (26)$$

The reasoning employed in the derivation of Eq. (25) may not be close to the real situation; however, it is interesting to note that the characteristic time of

the ozone variation in Eq. (25) is different by a factor of 1/4 from that in Eq. (20b). Another fact is that the ozone variation expressed by both Eqs. (20a) and (20b) indicates its increase with time, but Eq. (25) indicates its decrease with time. The actual photochemistry of the ozone is governed by many factors and reactions other than the simplified chemical reactions investigated here (Craig, 1965; Dütsch, 1961). Therefore the conclusion for the daytime ozone variation should not be drawn merely from the results obtained from Eqs. (20a), (20b) or (25).

b) Nighttime Variations. The nighttime variations in atomic oxygen and ozone are also investigated by using the same rate equations, Eqs. (6) and (8) but with the condition $J_2 = J_3 = 0$. Although this condition simplifies the equations, they remain quadratic with regard to $n(\text{O})$ and $n(\text{O}_3)$. There exists no photochemical equilibrium during the night since the roots of the equations are either zero or negative.

The nighttime rate equation of the atomic oxygen is

$$\frac{dn(\text{O})}{dt} = -2k_{11} n(\text{M}) n^2(\text{O}) - k_{12} n(\text{M}) n(\text{O}) n(\text{O}_2) - k_{13} n(\text{O}) n(\text{O}_3) \dots\dots\dots (27)$$

Below 60 km the second term in the right-hand side of the equation is predominant.

In the narrow region around 70 km the values of the three terms are similar in magnitude. In principle, therefore, no term can be eliminated, and the direct integration of Eq. (27) is practically impossible. A crude approximation is made by dropping the third term and by multiplying the first term by two, since the term values are almost identical. The use of this approximation makes it possible for the equation to be integrated. Between 80 and 100 km the contribution from the third term is quite negligible, since the controlling recombination processes at these levels are mainly due to the first and second terms. Above 100 km only the three-body recombination of atomic oxygen is responsible for the variation. The solutions of Eq. (27) at different levels are given by the following equations.

Below 60 km,

$$n(\text{O}) = n_i(\text{O}) e^{-k_{12} n(\text{M}) n(\text{O}_2) t} \dots\dots\dots (28)$$

The characteristic time for this solution is

$$\tau = [k_{12} n(\text{M}) n(\text{O}_2)]^{-1} \dots\dots\dots (29)$$

In the neighborhood of 70 km,

$$n(O) = n_i(O) e^{-k_{12} n(M) n(O_2) t} \left[\frac{k_{12} n(M) n(O_2)}{k_{12} n(M) n(O_2) + 4k_{11} n(M) n_i(O) (1 - e^{-k_{12} n(M) n(O_2) t})} \right]$$

τ for Eq. (30) is identical with τ in Eq. (29). Between 80 and 100 km the solution is the same as the formula given by Eq. (30), except for a numerical coefficient of 2 in stead of 4 in the second term of the denominator. For the formula for τ in Eq. (29) is also applicable to τ this case. Above 100 km, the atomic oxygen concentration is

$$n(O) = n_i(O) [1 + 2k_{11} n(M) n_i(O) t]^{-1} \quad (31)$$

The coefficient $2k_{11} n(M) n_i(O)$ is very small in magnitude, about 10^{-7} or less, when $n_i(O)$ is replaced by $n_e(O)$, indicating that in this region the atomic oxygen will remain at its initial value for the period of about a month.

The nighttime ozone varies through the rate equation of

$$\frac{dn(O_3)}{dt} = k_{12} n(M) n(O) n(O_2) - k_{13} n(O) n(O_3) \quad (32)$$

We assume that below about 75 km the atomic oxygen variation is efficiently represented by the equation

$$n(O) = n_i(O) e^{-k_{12} n(M) n(O_2) t} \quad (33)$$

Thus the substitution of the $n(O)$ formula into Eq. (32) makes the equation integrable, and we get the solution to Eq. (32) as

$$n(O_3) = n_i(O_3) \exp \left\{ - \frac{k_{12} n_i(O)}{k_{12} n(M) n(O_2)} (1 - e^{-k_{12} n(M) n(O_2) t}) \right\} + \frac{k_{12} n(M) n(O_2)}{k_{13}} \left[1 - \exp \left\{ - \frac{k_{12} n_i(O)}{k_{12} n(M) n(O_2)} (1 - e^{-k_{12} n(M) n(O_2) t}) \right\} \right] \quad (34)$$

For the period of time less than about 10^5 sec (about 1 day) $k_{12} n(M) n(O_2) t$ becomes equal to about 0.1 or less, and in the expansion of the exponential term the terms higher than the first order are neglected. Thus Eq. (34) is approximated to

$$n(O_3) = n_i(O_3) e^{-k_{12} n_i(O) t} + \frac{k_{12} n(M) n(O_2)}{k_{13}} (1 - e^{-k_{12} n(M) n(O_2) t}) \quad (35)$$

In both solutions the characteristic times have the formula

$$\tau = [k_{12} n_i(O)]^{-1} \quad (36)$$

The ozone concentration beyond the 80 km level diminishes rapidly with increased altitude, and it reaches an equilibrium value in a few hours or less,

as indicated by the values of Eq. (36) plotted in Fig. 5 b (curve II). The rate equation for this region is deduced from Eq. (32) by retaining only the first term, the three-body recombination of atomic and molecular oxygen into ozone. Since the corresponding variation in atomic oxygen concentration is described by Eq. (31), Eq. (32) reduces to

$$\frac{dn(O_3)}{dt} = k_{12} n(M) n(O_2) \left[\frac{n_i(O)}{1 + 2k_{11} n(M) n_i(O) t} \right] \quad (37)$$

The ozone concentration varies according to

$$n(O_3) \approx n_i(O_3) + k_{12} n(M) n(O_2) n_i(O) t \quad (38)$$

or

$$\approx n_i(O_3) + n_i(O) \quad (38)$$

In the derivation of Eq. (38) the conditions $2k_{11} n(M) n_i(O) t \ll 1$ and $k_{12} n(M) n(O_2) t \approx 1$ are assumed to hold. Eq. (38) indicates the upper limit value of $n(O_3)$. Similarly to the situation of the ozone variation in the lower atmosphere, the variation in $n(O_3)$ above 80 km is not merely controlled by the reactions studied in this paper, but as pointed out by many authors, the formation of hydroxyl radicals from the reaction between ozone and hydrogen becomes one of the important atmospheric reactions at this level.

The characteristic times associated with the daytime and nighttime variations in atomic oxygen and ozone are shown in Fig. 5 a and 5 b. The values of $(2Q)^{-1}$ and $[k_{12} n(M) n(O_2)]^{-1}$ calculated in this paper differ from Wallace's values by a factor of 4 or more, and the difference is mainly due to the differences in the atmospheric models and the rate constants adopted. As expected, the magnitude of Eq. (12) and Eq. (12a) are the same at lower region, and at the high altitudes Eq. (12) and Eq. (12c) lead to the same values for the characteristic times. The characteristic times expressed by $[k_{12} n(M) n(O_2)]^{-1}$, Eq. (15a) decrease rapidly and they approach the values of $(2Qa)^{-1}$ at the very low altitudes about the 30 km level.

The characteristic times associated with the variation in ozone represented by curve I (daytime) in Fig. 5 b, remain in a relatively constant value between 70 and 80 km. This result may be due to the neglect of some possible reactions of ozone with hydrogen.

IV. Numerical Solutions

Chemical reactions of a system of atmospheric

species are rate phenomena occurring simultaneously; therefore computations of the distribution of atmospheric gas concentrations (or photochemical equilibrium concentrations) and their time variations should be investigated by solving the rate equations simultaneously. However, if the rate equations contain terms of the second order reactions (nonlinear with respect to concentrations) as in Eqs. (6) and (8) the direct integration of the two equations is almost impossible unless some modification or approximation is made to the equations. Such difficulties involving Eqs. (6) and (8) were discussed by Craig (1965).

Leovy (1964) was able to solve the rate equations simultaneously by modifying the equations into the linearized forms: he substituted the initial value $n_i(O)$ for $n(O)$ in the nonlinear terms. Hunt (1965) reported the simultaneous integration of Eqs. (6) and (8) with the use of the four-point Runge-Kutta scheme for the height range of 47-80 km. In Hunt's work the initial values of $n(O)$ and $n(O_3)$ were not obtained, and it was necessary to repeat the integration using the new values until a stable state was reached, in which the values of $n(O)$ and $n(O_3)$ for a 24-hour period were the same as those for the same time on the preceding day. He found that the lower altitude regions rapidly stabilized while the high regions required several 24-hour iteration processes to attain a steady state.

In the present work on a CDC 6600 computer the initial equilibrium values (These are essentially photochemical equilibrium values, but we call them initial equilibrium values in this section in order to avoid the confusion with those in Section II.) of $n(O)$ and $n(O_3)$ are computed using the Newton-Raphson method (from Ralston, 1965) to solve two simultaneous nonlinear equations:

$$\begin{aligned} 2J_2n(O_2) + J_3n(O_3) - 2k_{11}n(M)n^2(O) \\ - k_{12}n(M)n(O)n(O_2) - k_{13}n(O)n(O_3) = 0 \cdots (39) \\ -J_3n(O_3) + k_{12}n(M)n(O)n(O_2) - k_{13}n(O)n(O_3) = 0 \end{aligned}$$

The values of $n(O)$ and $n(O_3)$ computed by this method agree closely with those of $n_e(O)$ and $n_e(O_3)$ calculated in Section II, the difference being less than 10% in most cases. The fourth order Runge-Kutta integration method (from Ralston, 1965), used also by Hunt, is employed to integrate Eqs. (6) and (8)

simultaneously. The integration was performed starting from the noon hour with the 24-hour iteration cycle. The initial equilibrium values obtained from the Newton-Raphson method are used as the starting values in this integration. The values obtained from the integration for 24-hour and 48-hour periods were averaged with the initial equilibrium values, and the iteration was repeated until stable steady-state values are attained. Time steps of 1 minute, 3 minutes, 5 minutes, and 15 minutes were employed. The results obtained from the 1-minute iteration were used to investigate the variation in concentration at sunset and sunrise. As the time step was increased the integration became more unstable; for instance, the time interval of 5 minutes or larger failed to show stable integration below 65 km whereas the time step of 1 minute allowed stable integration down to 50 km. Also in the region lower than 55 km the variation in atomic oxygen after sunset changes very rapidly and its concentration reached zero in a short time; for example, at 50 km the atomic oxygen concentration changed from 2.44×10^{10} (molecules, cc^{-1}) to zero in a 15-minute interval. This variation is in good agreement with the result obtained in Section III, in which the characteristic time of the nighttime atomic oxygen variation at this level was found to be about 20 sec.

Similar to Hunt's, result it was found that in the region between 50-70 km atomic oxygen and ozone reached their state rapidly within one 24-hour cycle and between 75-100 km it required longer periods. Above 100 km it was also found that one 24-hour cycle iteration was again sufficient to bring $n(O)$ and $n(O_3)$ to their steady state values. Fig. 6 shows the ratio of photochemical equilibrium concentrations to initial equilibrium concentrations obtained from the Newton-Raphson method and the ratio of nonequilibrium concentrations, obtained from the Runge-Kutta method to initial equilibrium concentrations.

V. Discussion

In sections II, III, and IV calculations of the concentration profiles of atomic oxygen and ozone were performed under the condition of photochemical equi-

rium, by making modifications and approximations to the rate equations, and by solving the equations simultaneously with numerical methods. Calculations were also performed on the time variations in atomic oxygen and ozone at various altitudes under the under the latter two provisions.

Fig. 1 and 2 indicate that some discrepancies exist the values of J_2 and J_3 between those adopted in this paper and those calculated by Catchpole. Catchpole's values for J_2 near the 80 km region are smaller by an

order of magnitude than those employed in the present calculation, and his J_3 values are found to be larger by a factor of about 3 in the entire region. J_2 appears in the $n_e(O)$ formula as $(J_2)^{1/2}$ and J_3 in $n_e(O_3)$ as $1/J_3$ in the region above 60 km, and below this level the $n_e(O)$ and $n_e(O_3)$ formulas contain the factors $(J_2 J_3)^{1/2}$ and (J_2/J_3) , respectively. Therefore, the influence of J_2 and J_3 on the number densities of O and O_3 can be easily estimated.

The comparison between the results of the present

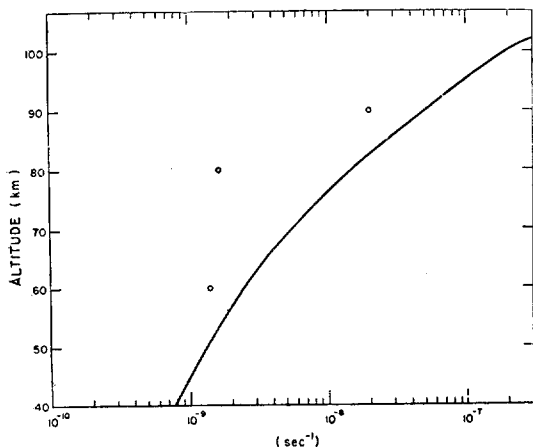


Fig. 1a. Photodissociation Rate of Molecular Oxygen (sec^{-1})

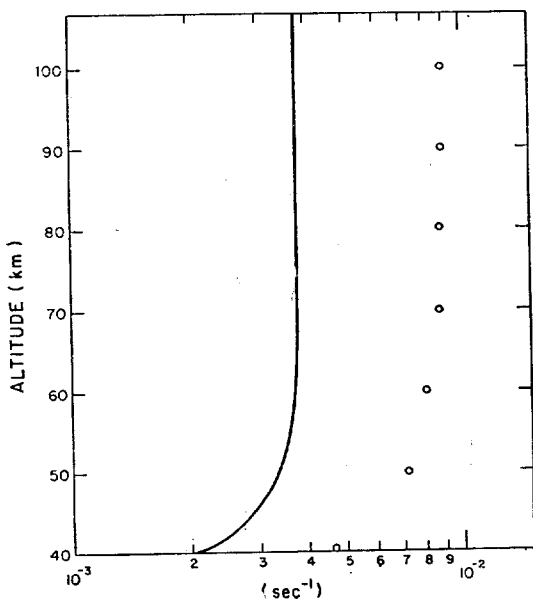


Fig. 1b. Photodissociation Rate of Ozone (sec^{-1})

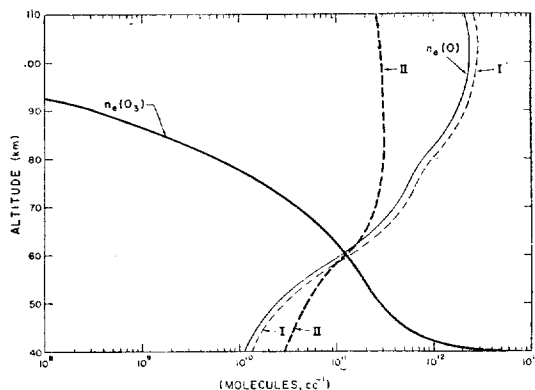


Fig. 2. Photochemical Equilibrium Concentrations of Atomic Oxygen and Ozone (molecules, cc^{-1}) I. $n_e(O)$ calculated using $n(M) = n(O_2) + 0.6n(N_2)$ II. $n_e(O)$ calculated using fixed values for J_2 and J_3

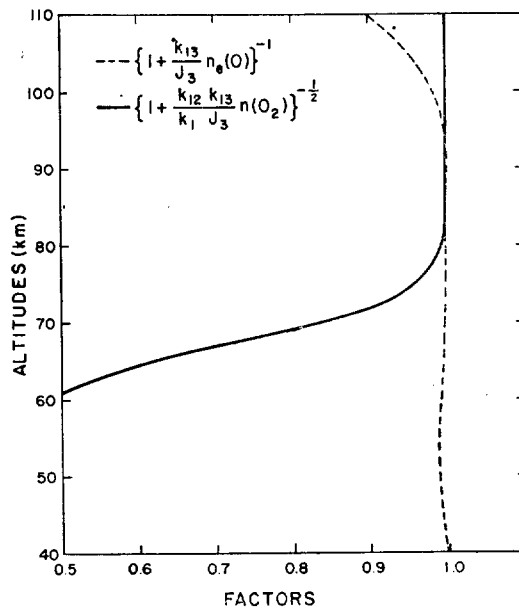


Fig. 3. Factors Involved in the Photochemical Equilibrium Concentration Formulas

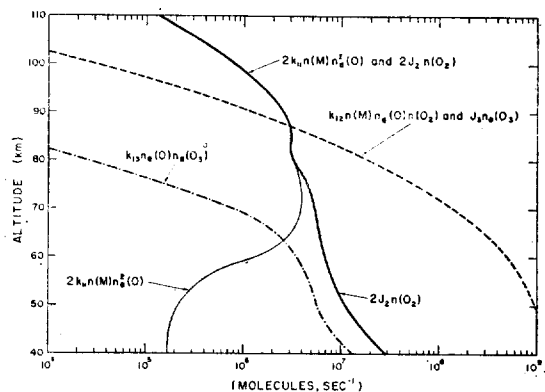


Fig. 4. Magnitudes of the Term Values in Eqs. 6 and 8

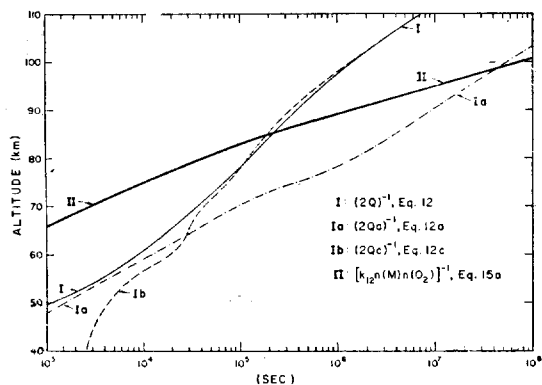
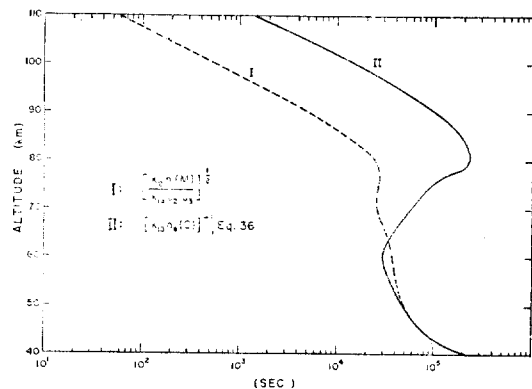
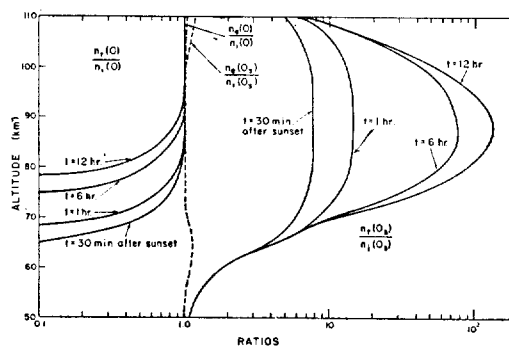
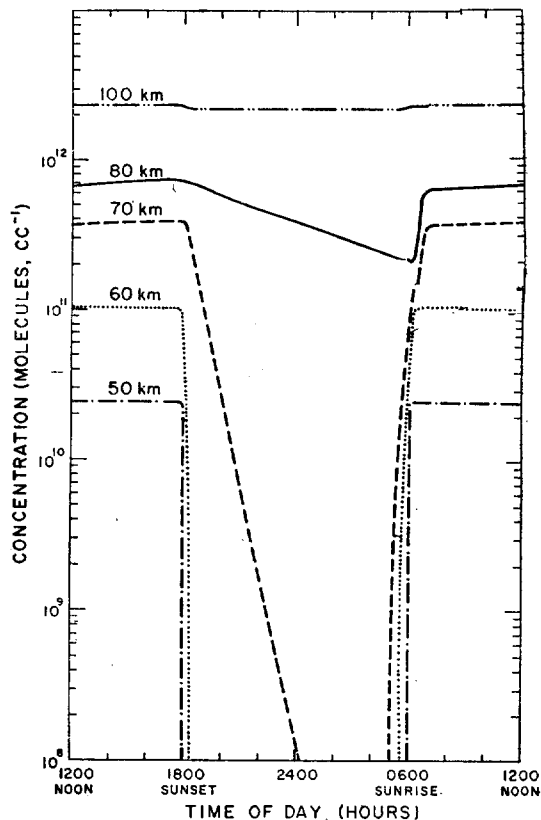
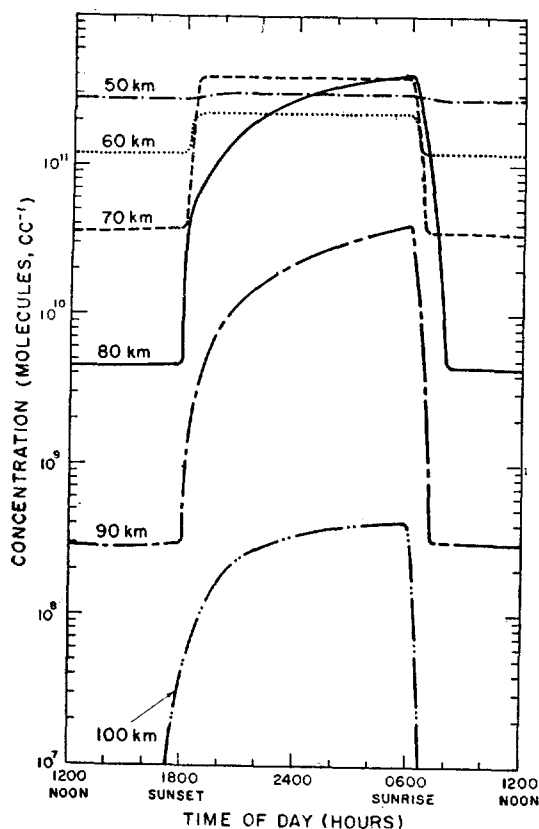
Fig. 5a. Characteristic Times for Variations in $n(O)$ (sec)Fig. 5b. Characteristic Times for Variations in $n(O_3)$ (sec)

Fig. 6. Ratios of Photochemical Equilibrium Concentrations to Initial Equilibrium Concentrations and Nonequilibrium Concentration to Initial Equilibrium Concentrations

Fig. 7a. Variations in $n(O)$ for a 24-Hour Period

calculation and those of other investigators are made in Fig. 8a and 8b. Fig. 8b indicates that theoretical calculations usually yield higher values of the photochemical equilibrium distribution of ozone than those

observed. As pointed out by a number of investigators such high values may have resulted from the neglect of some possible reactions between ozone and excited species of atomic and molecular oxygen and between

Fig. 7b. Variations in $n(\text{O}_3)$ for a 24-Hour Period

ozone and OH radicals. In the lower atmosphere the reactions of oxygen allotropes with NO , NO_2 , and water vapor are quite significant; during the night at 70 to 90 km levels, the formation of hydroxyl radicals from the reaction between ozone and atomic hydrogen is important and is responsible for the OH night glow emission observed at these levels. Studies on the nonequilibrium effects as an extended system including hydrogen compounds have also appeared in the recent literature (Wallace, 1962; Hunt, 1966; Leovy, 1966).

The disagreement found in the number densities of atomic oxygen and ozone between the present work and others is largely attributed to the fact that the values of J_2 and J_3 used by various authors are substantially different since the accurate values are not well established. However, owing to the many recent critical studies on the relevant reaction rate constants and

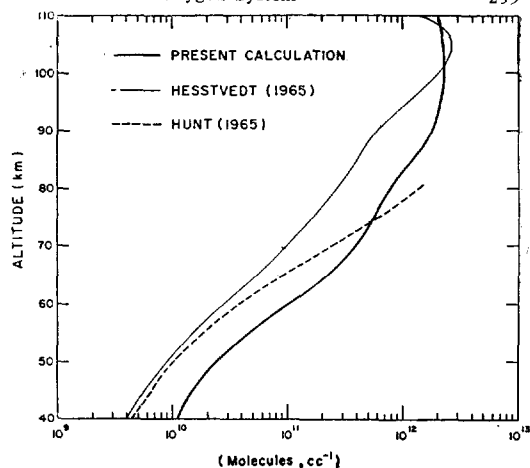


Fig. 8a. Comparison of Photochemical Equilibrium Atomic Oxygen Concentrations

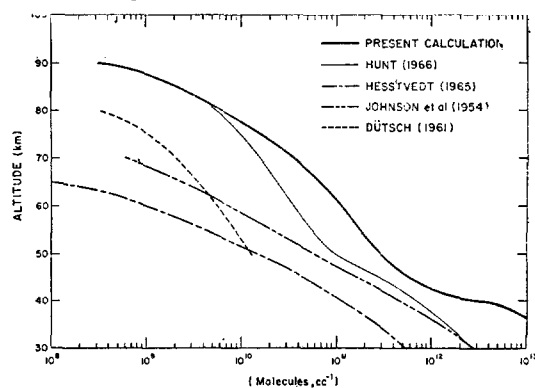


Fig. 8b. Comparison of Photochemical Equilibrium Ozone Concentrations

mechanisms, the values of the rate coefficients k_{11} , k_{12} , and k_{13} adopted in the study of atmospheric chemical reactions are fairly consistent among investigators. At present accurate J_2 and J_3 are highly desirable; improvements for the accuracy of these constants mainly depend on the precise measurement of the energy distribution of the solar spectrum.

In Table 2 are listed the values of the reaction rate constants employed by several authors for the calculation of the photochemical equilibrium densities of atomic oxygen and ozone. A comparison is also made, in Table 3, for the time variation of the ozone distribution for the 24-hour period with other calculated results appeared in literatures, and the values listed in this table are estimated from data reported in the literatures.

The calculations in this paper were performed for

TABLE 2. Reaction Rate Constants

	Hessvedt (1965)	Hunt (1966)	Leovy(1964)	Present work
k_{11}	$1.6 \times 10^{-34} T^{1/2}$	2.7×10^{-33}	2.7×10^{-33}	$5.0 \times 10^{-34} T^{1/2}$
k_{12}	$6.4 \times 10^{-36} T^{1/2}$	$5 \times 10^{-35} \exp(1000/RT)$	1.2×10^{-34}	$7.5 \times 10^{-35} \exp(890/RT)$
k_{13}	$4.2 \times 10^{-13} T^{1/2}$	$5 \times 10^{-11} \exp(-5600/RT)$	$1.5 \times 10^{-10} \exp(-3025/T)$	Averaged Formula given in Sect. II

TABLE 3. Comparison of the Diurnal Variation of Ozone Concentrations (Molecules, cc^{-1})

	Altitude (km)	06 : 00 Sunrise	08 : 00	12 : 00 Noon	16 : 00	18 : 00 Sunset	20 : 00	24 : 00 Midnight	04 : 00
Hunt(1965)	48	4.4×10^{10}	4.2×10^{10}	4.0×10^{10}	4.1×10^{10}	4.6×10^{10}	4.6×10^{10}	4.6×10^{10}	4.6×10^{10}
Leovy(1964)	49	5.2×10^{10}	4.6×10^{10}	4.5×10^{10}	4.7×10^{10}	5.1×10^{10}	5.5×10^{10}	5.8×10^{10}	5.8×10^{10}
Present work	50	2.9×10^{11}	2.8×10^{11}	2.8×10^{11}	2.8×10^{11}	2.8×10^{11}	3.0×10^{11}	3.0×10^{11}	3.0×10^{11}
Hunt	58.75	2.0×10^{10}	7.7×10^9	1.1×10^{10}	9.5×10^9	1.5×10^{10}	2.4×10^{10}	2.4×10^{10}	2.4×10^{10}
Leovy	61	2.1×10^{10}	7.0×10^9	8.0×10^{10}	8.7×10^9	1.3×10^{10}	3.5×10^{10}	3.6×10^{10}	3.6×10^{10}
Present work	60	2.0×10^{11}	1.2×10^{11}	1.2×10^{11}	1.2×10^{11}	1.2×10^{10}	2.2×10^{11}	2.2×10^{10}	2.2×10^{11}
Hunt	68.75	1.5×10^{10}	1.4×10^9	2.6×10^9	3.3×10^9	4.4×10^9	5.1×10^{10}	5.1×10^{10}	5.1×10^{10}
Leovy	67	1.0×10^{10}	2.5×10^9	3.8×10^9	4.2×10^9	4.6×10^9	5.5×10^{10}	5.8×10^{10}	5.8×10^{10}
Present work	70	3.6×10^{11}	3.6×10^{11}	3.4×10^{10}	3.6×10^{10}	3.8×10^{10}	3.7×10^{11}	3.9×10^{11}	3.9×10^{11}

the condition that the sun is at the overhead position, the zenith angle being zero for the daytime variation. This simplified assumption leads to the results that the photodissociation rates deviate from the real values most widely at sunrise and sunset, thus introducing more uncertainty in the dissociation rate constants. Discussions of the perturbation in photodissociation rates due to sun position and to other factors are referred to in the literature (Leovy, 1966; Craig, 1965).

ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. R. D. Cadle for suggesting this problem and for his continuous encouragement. Thanks are due also to the staff of the Computing Facility of NCAR, and especially to L. Higbie, for generous assistance in programming.

REFERENCES

- 1) Bates, D. R., and M. Nicolet, 1950: *J. Geophys. Res.* **55**, 301.
- 2) Barth, C. A., 1961: *Chemical Reactions in the Lower and Upper Atmosphere*, pp. 303-326, Interscience Publ.
- 3) Catchpole, J. R., 1964: *J. Atmospheric Terrest. Phys.* **26**, 1007.
- 4) Chapman, S., 1930: *Phil. Mag.* **7**, 10, 369.
- 5) CIRA, 1965: *COSPAR International Reference Atmosphere*, North-Holland Publ. Co.
- 6) Craig, R. A., 1965: *The Upper Atmosphere, Meteorology and Physics*, Ch. 5, Academic Press.
- 7) *Ibid.*, Appendix D.
- 8) Dütsch, H. U., 1961: *Chemical Reactions in the Lower and Upper Atmosphere*, pp. 167-180, Interscience Publ.
- 9) Hessvedt, E., 1965: *Geof. Publ.* **XXVI**, No. 1.
- 10) Horiuchi, G., 1961: *Geophys. Mag.* **30**, 439.
- 11) Hunt, B. G., 1965: *J. Atmospheric Terrest. Phys.* **27**, 133.
- 12) Hunt, B. G., 1966: *J. Atmos. Sci.* **23**, 88 and *J. Geophys. Res.* **71**, 1385.
- 13) Johnson, F. S., J. D. Purcell, and R. Tousey, 1954: *Rocket Exploration of the Upper Atmos-*

- phere, R. L. E. Boyd and M. J. Seaton, ed., pp. 189-199, Pergamon Press.
- 14) Leovy, C. B., 1964: *J. Atmos. Sci.* **21**, 238.
- 15) Leovy, C. B., 1966: *J. Atmos. Sci.* **23**, 223.
- 16) Nawrocki, P. J., and R. Papa, 1963: *Atmospheric Processes*, Chapters 1 and 2, Prentice-Hall, Inc.
- 17) Nicolet, M., and P. Mange, 1954: *J. Geophys. Res.* **59**, 15; and also M. Nicolet, Ch. 11 in *Physics of Upper Atmosphere*, J. A. Ratcliffe, ed., Academic Press, 1960. Earlier works and works done by other authors are referred to in the references quoted therein.
- 18) Nicolet, M., 1964: *Disc. Faraday Soc.* No. 37, 7.
- 19) Nicolet, M., 1965: *Proc. Roy. Soc., London* **A288**, 479.
- 20) Penndorf, R., 1949: *J. Geophys. Res.* **54**, 7.
- 21) Ralston, A., 1965: *A First Course in Numerical Analysis*, McGraw-Hill Book Co.
- 22) Schofield, K., 1967: *Planet. Space Sci.* **15**, 643.
- 23) Wallace, L., 1962: *J. Atmos. Sci.* **19**, 1.
- 24) Watanabe, K., 1958: *Advances in Geophysics*, Vol. 5, Academic Press.
- 25) Wulf, O. R. and L. S. Deming, 1936: *Terr. Mag.* **41**, 299 and 375.
- 26) Young, C., and E. S. Epstein, 1962: *J. Atmos. Sci.* **19**, 435.