INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE

3, avenue Circulaire, UCCLE - BRUXELLES 18

AERONOMICA ACTA

A - N° 28 - 1964

Introduction to chemical aeronomy

by M. NICOLET

FOREWORD

"Introduction to Chemical Aeronomy" is the introduction text which had to be used for general discussion at the Faraday Society in Edinburgh on April 2-3, 1964.

AVANT-PROPOS

"Introduction to Chemical Aeronomy" est le texte d'introduction devant servir à la discussion générale de la Faraday Society à Edinburgh, Avril 2-3, 1964.

VOORWOORD

"Introduction to Chemical Aeronomy" is de inleidende tekst tot een algemene bespreking van de Faraday Society welke gehouden werd te Edinburgh op 2 en 3 April 1964.

VORWORT

"Introduction to Chemical Aeronomy" is der Einleitungs- text,der zur general Diskussion der Faraday Society in Edinburgh am 2.-3. April 1964 benutzt wurde.

INTRODUCTION TO CHEMICAL AERONOMY

by

Marcel NICOLET

Centre National de Recherches de l'Espace,
3, Avenue Circulaire,
BRUXELLES 18.

1.- Introduction.

Thirty-three years ago, Chapman[1] demonstrated that the dissociation of molecular oxygen is important above 100 km, and, therefore, that the photo-chemistry of atmospheric oxygen [2] is an important problem in aeronomy. However, the treatment of oxygen dissociation at high altitude must be examined[3] by studying the departure from photochemical equilibrium conditions. In fact, any detailed investigation requires a knowledge of aeronomic conditions in the various atmospheric regions.

Theoretical studies are simplified by dividing the atmosphere into two parts : the homosphere, in which the composition of the principal constituents ($N_2 \simeq 78°/_o$, $O_2 \simeq 21°/_o$ and $A \simeq 1°/_o$) remains constant and the heterosphere, in which the dissociation of oxygen and diffusion affect the air composition. If the temperature distribution is introduced as the second aeronomic parameter, the homosphere is subdivided in three regions : The lowest region is the troposphere where the temperature decreases with height up to the tropopause. The tropopause has a temperature of about 220°K in the polar regions at a height of some 8 km and about 190°K at the equator for an altitude of the order of 17 km. The stratosphere is essentially that region where the temperature increases or at least does not decrease, with altitude. It extends from the tropopause to an altitude of about of 50 km where the temperature reaches a peak of the order of 273°K. The third region belonging to the homosphere is the mesosphere situated between the stratopause(50 ± 5 km) and the mesopause (85 ± 5 km) where the temperature reaches a minimum as low as 160 - 170°K. Above the mesopause, there is an increase of the temperature which has its largest gradient (up to 20° km^{-1}) near 150 km. In this region, the thermosphere, the problems of the chemosphere change in that ionisation must be considered along with dissociation.

The vertical distribution of atomic oxygen makes it possible to understand the different roles of the three regions of the homosphere and the heterosphere. In the thermosphere atomic oxygen is more abundant than molecular oxygen above about 120 km. In the mesosphere, atomic oxygen is more abundant than ozone for an atmosphere illuminated by the sun. The day and night-time conditions are different. In the stratosphere, atomic oxygen is always less abundant than ozone, the presence of which depends on photochemical reactions. Finally, ozone is a permanent element of the air mass in the troposphere and is subject to variations associated with advective and dynamical transport.

After considering the principal constituents, it is necessary for chemical aeronomy to introduce the minor constituents. An inert gas such as helium (ratio 5.24×10^{-6} per volume) which has no chemical importance is, however, a tracer for atmospheric diffusion processes since it is not a minor constituent in the upper thermosphere. Several of the minor constituents observed at ground level (Table I) can play a role in the chemosphere. No systematic study of their abundance has been made at high altitudes and their behavior is known from infrared spectroscopic identifications or from chemical analysis at low levels.

TABLE I : Molecular content of minor constituents.

Molecule	Ratio by volume	Remarks
CO_2	3×10^{-3}	Mixed in the troposphere, small variation.
H_2O	10^{-5} to 10^{-2}	Variable. Dissociation in mesosphere.
O_3	10^{-7} to 10^{-8}	Variable. Peak in stratosphere.
CH_4	1.5×10^{-6}	Mixed in troposphere. Dissociation in mesosphere.
N_2O	5×10^{-7}	Mixed in troposphere. Dissociation in stratosphere.
H_2	5×10^{-7}	Mixed in troposphere. Dissociation in thermosphere.
CO	5×10^{-8} to 2×10^{-7}	Variable. Industrial.
NO_2-NO	5×10^{-10} to 2×10^{-8}	Variable. Industrial. Chemical origin in mesosphere and thermosphere.

The photochemistry of atmospheric water vapor was studied in considerable detail by Bates and Nicolet [4] after Meinel [5] discovered that the vibrational rotational bands of the hydroxyl radicle OH appear in the airglow with a total energy [6] of about 3 ergs $cm^{-2}sec^{-1}$. Such an emission arouses interest in the photochemistry of hydrogen - oxygen compounds [7], not only of water vapor but also of methane and perhydroxyl radicles. The attack of methane by atomic oxygen was studied by Bates and Witherspoon[8] and there is little doubt that the concentration of methane in the mesosphere depends on collision processes involving atomic oxygen. The enteric fermentation corresponds to a production [9] of CH_4 of at least 10^{10} molecules cm^{-2} sec^{-1}. The chemical oxidation of methane in the stratosphere leads to a production of hydrogen , the accumulation of which is limited by the possibility of the upward transport into the mesosphere.

Unlike oxygen, nitrogen is extremely difficult to dissociate and it is so stable that it remains in the molecular form up to very great altitude. This low degree of dissociation was suggested [10] in studies of nitric oxide which was considered to be an important ionic constituent of the terrestrial ionosphere. The photochemistry of tropospheric nitrous oxide has been investigated by Bates and Witherspoon [8] who indicated that this molecule is not a member of the main photochemical family of nitrogen oxides which were studied by Bates [11] and Nicolet[12, 13]. Free nitrogen atoms in an oxygen atmosphere make possible a large number of reactions which are now studied in the laboratory.

A difficulty in giving a systematic account of the chemical aeronomy has been the grevious lack of reliable basic data. Our knowledge concerning the experimental rate coefficients has increased rapidly however in recent years and systematic accounts can be found in several review papers presented at the symposium on aeronomy held in Berkeley in August 1963: Three-body reactions by Barth [14]; Reactions involving nitrogen and oxygen by Schiff [15] and Aeronomic reactions involving hydrogen by Kaufman [16]. Much progress must still be made in the elucidation of chemical reactions for a complete application to aeronomy. It cannot be overemphasized that laboratory

investigations under controlled conditions are of fundamental importance for an useful interpretation of space observations.

2.- Solar radiation and its absorption.

A knowledge of the radiation available for dissociation in the atmosphere is required before conclusions can be reached regarding the relative importance of aeronomic processes. The principal gases in the thermosphere, molecular nitrogen, atomic oxygen and molecular oxygen, limit the penetration of solar radiation into the heterosphere at wavelengths $\lambda < 796A$, $\lambda < 910A$ and $\lambda < 1025A$, respectively. Since absorption cross-sections are not less than 10^{-18} cm^2 between 1000 A and 100 A, the solar radiation in this spectral range is absorbed above 100 km and ionizes N_2, O and O_2. The total number of solar photons available at the top of the earth's atmosphere is not greater than 2×10^{11} photons cm^{-2} sec^{-1}, and corresponds to the number of ionizing processes in the E and F ionospheric layers. Molecules such as NO_2, H_2O, O_3, N_2O, CH_4 and OH can be neglected in the study of the ionization of the atmosphere since their ionization potential is greater than that of molecular oxygen. No radiation will be available to ionize these molecules below 100 km where they are subject to dissociation processes.

At 1750 A (see Fig. 1) where the Schumann-Runge continuum of molecular oxygen begins, the total number of photons available at the top of the earth's atmosphere is of the order of 2×10^{12} photons $cm^{-2} sec^{-1}$ and consequently this value also represents the total number of oxygen molecules which is dissociated in a vertical column of the atmosphere for $\lambda < 1750$ A.

At 2420 A where the Herzberg continuum of O_2 begins, the total number of solar photons is about 2.7×10^{14} photons $cm^{-2} sec^{-1}$ and such a value corresponds to the maximum number of oxygen molecules which could be dissociated per cm^2 sec^{-1} in a vertical column of the earth's atmosphere. Thus the number of photodissociation processes of molecular oxygen $D(O_2)$ in the earth's atmosphere is

$$2 \times 10^{12} < D(O_2) < 2.7 \times 10^{14} \; cm^{-2} \; sec^{-1} \; . \tag{1}$$
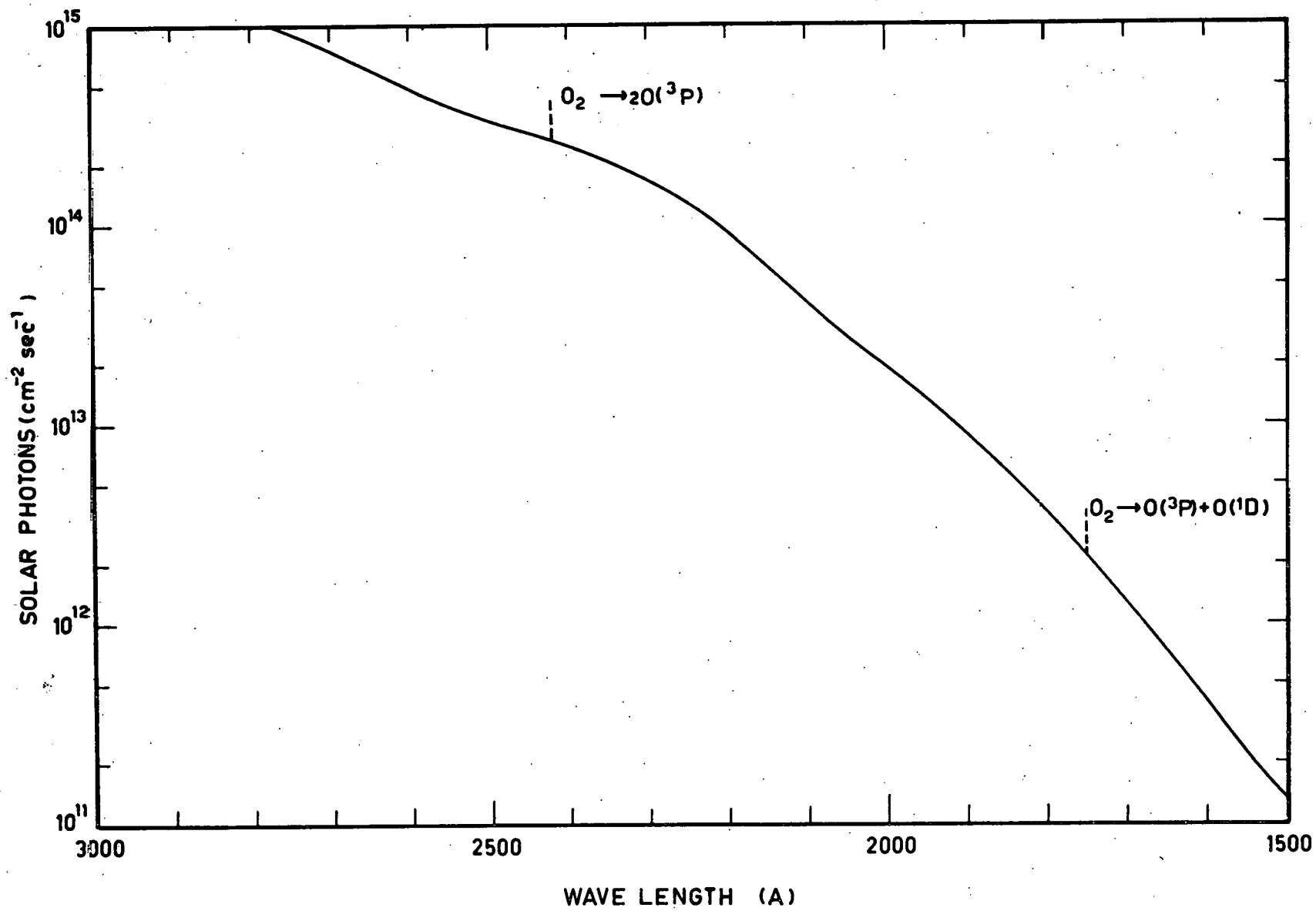
FIGURE 1.

The maximum value which can be reached depends on ozone absorption which needs be taken into account in estimating the dissociation rate in the Herzberg continuum. Ozone shows an important absorption which begins near 3500 A, extends below 3000 A with rapidly increasing cross-section to a maximum at about 2550 A, and is still important in the Herzberg continuum, $\lambda < 2400$ A. Due to the presence of O_3 molecules, it will be shown that the rate of dissociation of O_2 is strongly affected below the stratopause. Under these conditions, the dissociation of molecular oxygen must be studied before determining the behavior of other constituents.

The photodissociation process

$$O_2 + h\nu \ (\lambda \leq 1750 \ A) \ \rightarrow \ O(^3P) + O(^1D) \tag{2}$$
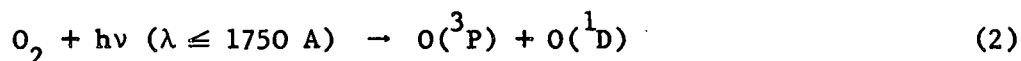
leads to a photodissociation rate coefficient J_{O_2} of the order of

$$J_{O_2} \ (\lambda \leq 1750 \ A) = 5 \times 10^{-6} \sec^{-1} \tag{3}$$

at zero optical depth.

The continuum of the Schumann-Runge system has an absorption cross-section varying from about 2×10^{-19} cm^2 at the threshold with a peak not less than 10^{-17} cm^2 between 1500 A and 1400 A. The penetration of solar radiation into the atmosphere is limited where the total content of O_2 molecules is between 10^{19} cm^{-2} and 10^{17} cm^{-2}. For example, a vertical column of 2×10^{18} O_2 molecules cm^{-2} (about 100 km) leads to photodissociation rate.

$$J_{O_2} \ (z \sim 100 \ km) = 2 \times 10^{-7} \ \sec^{-1} \ . \tag{4}$$

Thus the life-time of an oxygen molecule in the sun's radiation field is very long at heights where photochemical equilibrium conditions should be applied if transport process are ignored.

The penetration of solar radiation to greater depths than 10^{19} molecules cm^{-2} occurs only in various "windows" between 1225 A and 1100 A. The most important "window" is situated at 1216 A of the important solar

radiation, Lyman-α, for which the unit optical depth corresponds to a cross-section of the order of $10^{-20} cm^2$. Since the number of photons available in Lyman-α is between 2 and 4 x 10^{11} photons $cm^{-2} sec^{-1}$, the dissociation rate coefficient is

$$J_{O_2} (Ly-\alpha) = 2 \text{ to } 4 \times 10^{-9} sec^{-1} . \tag{5}$$

For an overhead sun, the dissociation rate coefficient at 75 km becomes

$$J_{O_2} (Ly-\alpha)_{75 \text{ km}} \simeq 10^{-9} sec^{-1} . \tag{6}$$

Since the concentrations of molecular oxygen at 75 km $n(O_2) \simeq 2 \times 10^{14} cm^{-3}$, the minimum dissociation rate is still $2 \times 10^5 cm^{-3} sec^{-1}$.

A difficulty occurs, however, in the determination of oxygen dissociation in the mesosphere. This difficulty comes from the impossibility of obtaining a sufficiently accurate value for aeronomic purposes. The dissociation rate in the Herzberg continuum, particularly near 2000 A where the Schumann-Runge bands occur, is not sufficiently precise[18]; we cannot enter into details here and an approximate distribution has been deduced (Fig. 2). A plot of J_{O_2} against height between 50 km and 100 km refering to an overhead sun indicates that J_{O_2} decreases by about a factor of 100 in this 50 km height interval. The effect of the Schumann-Runge continuum is apparent in the thermosphere and the decrease of J_{O_2} in the mesosphere is related to the absorption in the Herzberg continuum.

The photolysis of ozone is due to the absorption in the ultraviolet and the visible. It is customary to take absorption cross-sections as dissociation cross-sections and to adopt average numerical values for aeronomic purposes. It should be pointed out, however, that errors of about 10 percent still seem to occur in recent data[19, 20, 21]. In applying average values, the total rate coefficient J_{O_3} at zero optical depth is about
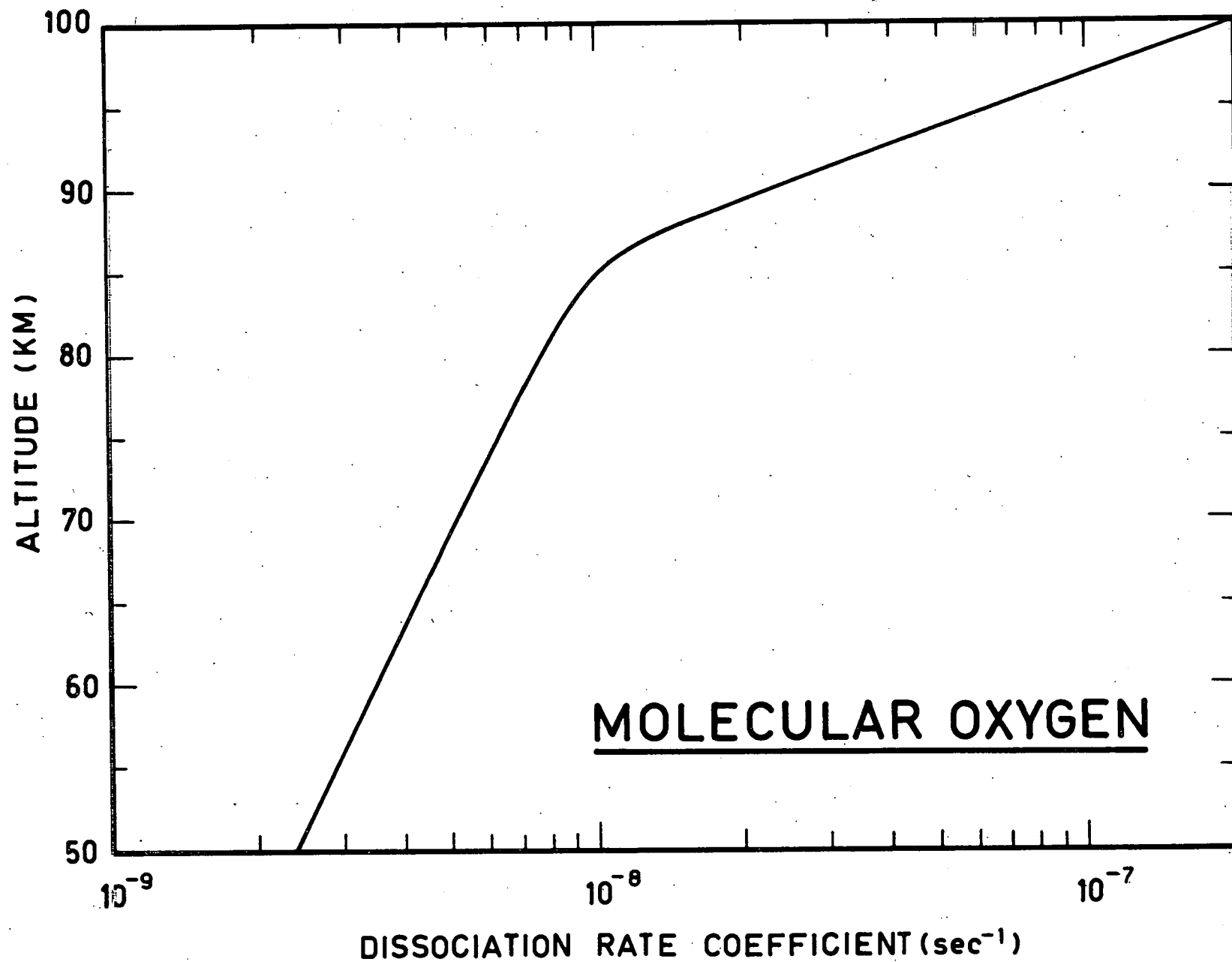
$$J_{O_3} = 10^{-2} sec^{-1} \tag{7}$$

FIGURE 2.

while the visible part of the spectrum leads to only

$$J_{O_3} \text{ (visible)} = 3.5 \times 10^{-4} \text{ sec}^{-1} . \tag{8}$$

It can be assumed that ozone and molecular oxygen are the two molecules which absorb solar radiation between 3000 A and 1000 A, i.e. that the other constituents constitute a negligible role.

Photodissociation of water vapor, which begins around 2400 A, is related to the absorption of molecular oxygen. The absorption cross-sections is less than 10^{-20} cm^2 at 1900 A (see Fig. 3) and increases rapidly in the spectral range of the Schumann-Runge bands system. It reaches about 10^{-18} cm^2 near 1800 A. Thus the photodissociation of H_2O in the mesosphere is related to the complicated structure of the absorption spectrum of O_2. At the present time, only a rough estimate can be obtained. The total dissociation rate coefficient at zeroth optical depth J_{H_2O} is about

$$J_{H_2O} = 10^{-5} \text{ sec}^{-1} \tag{9}$$

which becomes about 10^{-6} sec^{-1} near the mesopause level after absorption in Schumann-Runge bands. It is still about 10^{-6} sec^{-1} in the middle mesosphere due to the effect of solar Lyman-α. With such low values for the dissociation rate coefficients it is difficult to consider photochemical equilibrium conditions for water vapor in the mesosphere. The life time of water vapor in the solar radiation field is sufficiently long to lead to departures from photoequilibrium conditions.

Fig. 3 shows also the absorption cross-section of CO_2. Its photo-dissociation in the mesosphere is related to the effect of Lyman -α which leads to the following value of J_{CO_2},

$$J_{CO_2} \text{ (Lyman-}\alpha\text{)} = 3 \times 10^{-8} \text{ sec}^{-1}. \tag{10}$$
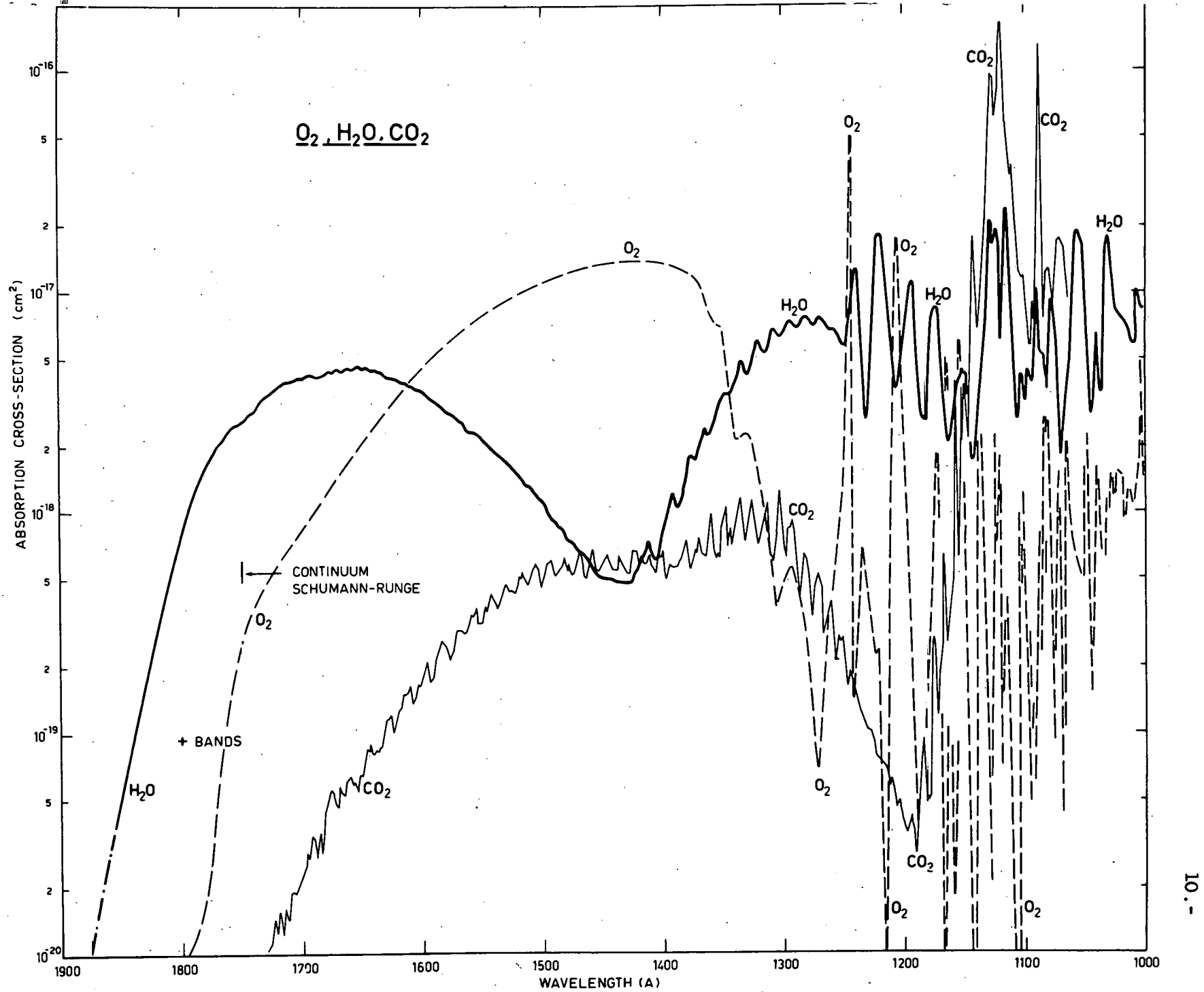
FIGURE 3.

Methane also has an absorption spectrum in the region of the Schumann-Runge continuum of O_2 and its direct photodissociation in the mesosphere depends on the penetration of Lyman-α. At zero optical depth, it is

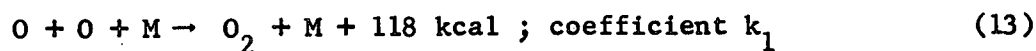$$J_{CH_4}(\text{Lyman-}\alpha) = 5 \times 10^{-6} \text{ sec}^{-1} \qquad (11)$$

Even if collisions involving atomic oxygen are effective as a loss process for methane in the mesosphere, photodissociation by Lyman-α at 75 km is sufficient to reduce its initial concentration to 50 percent in about 3 days of 12 hours.
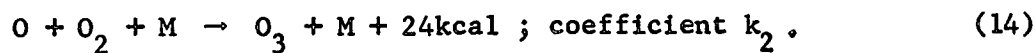
3.- Pure Oxygen Atmosphere.

The photochemistry of an oxygen atmosphere has been studied by a number of investigators (see for example [4, 22, 23]) since Chapman[1] gave the complete set of equations. We follow here the analysis made by Bates and Nicolet [4]. The dissociation of oxygen obtained by photodissociation
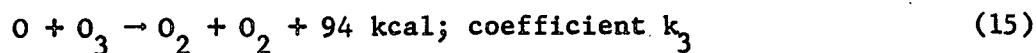
$$O_2 + h\nu(\lambda < 2420A) \rightarrow O + O; \text{ coefficient } J_{O_2} \qquad (12)$$

is followed by the three-body recombination

$$O + O + M \rightarrow O_2 + M + 118 \text{ kcal }; \text{ coefficient } k_1 \qquad (13)$$

and by

$$O + O_2 + M \rightarrow O_3 + M + 24\text{kcal }; \text{ coefficient } k_2. \qquad (14)$$

The bimolecular process occurs, therefore,

$$O + O_3 \rightarrow O_2 + O_2 + 94 \text{ kcal}; \text{ coefficient } k_3 \qquad (15)$$

and of course the photolysis of ozone is considered

$$O_3 + h\nu \rightarrow O_2 + O ; \text{ coefficient } J_{O_3}. \qquad (16)$$
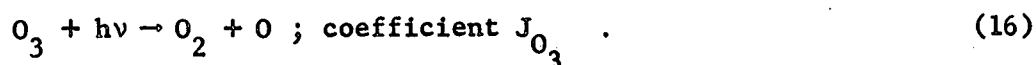
The equations governing the rate of charge of the concentrations $n(O_2)$, $n(O)$ and $n(O_3)$ are

$$\frac{dn(O_2)}{dt} + n(O_2)J_2 + k_2\, n(M)\, n(O_2)\, n(O) =$$

$$k_1\, n(M)\, n^2(O) + 2k_3\, n(O_3)\, n(O) + n(O_3)\, J_3 \qquad (17)$$

$$\frac{dn(O)}{dt} + 2k_1\, n(M)\, n^2(O) + k_2\, n(M)\, n(O_2)\, n(O) + k_3\, n(O_3)\, n(O) =$$

$$2\, n(O_2)\, J_2 + n(O_3)\, J_3 \qquad (18)$$

$$\frac{dn(O_3)}{dt} + n(O_3)\, J_3 + k_3\, n(O)\, n(O_3) = k_2\, n(M)\, n(O_2)\, n(O) \qquad (19)$$

The conditions for the simultaneous variation of $n(O)$ and $n(O_3)$ can be conveniently written

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1\, n(M)\, n^2(O) + 2k_3\, n(O_3)\, n(O) = 2\, n(O_2)J_2 \qquad (20)$$

At sufficiently high altitudes, i.e. in the thermosphere, (20) becomes, $n(O_3) \ll n(O)$,

$$\frac{dn(O)}{dt} + 2k_1\, n(M)\, n^2(O) = 2n(O_2)\, J_2 \qquad (21)$$

For the day equilibrium of ozone in the mesosphere,

$$\frac{dn(O)}{dt} + 2k_1 \, n(M) \, n^2(O) + 2k_3 \, n(O_3) \, n(O) = 2n(O_2)J_2 \tag{22}$$

In the stratosphere, the day-time conditions become, $n(O) \ll n(O_3)$,

$$\frac{dn(O_3)}{dt} \simeq 2n(O_2) \, J_2 \tag{23}$$

indicating that the equilibrium condition for ozone,

$$n^2(O_3) = \frac{k_2}{k_3} \, n(M) \, n^2(O_2) \, \frac{J_2}{J_3} \quad , \tag{24}$$

is reached depending on

$$n_t(O_3) = n_{t_o}(O_3) + 2n(O_2) \, J_2 \cdot t \quad , \tag{25}$$

t being the time measured from an initial time t_o. The time t increases with lower heights since the dissociation rate coefficient J_2 decreases more rapidly than $n(O_2)$ increases. Departure from photochemical equilibrium conditions takes of the order of several days below 40 km. Any variation in the ozone content of the stratosphere modifies the value of J_2 and affects the vertical distribution of ozone.

If numerical values of the various parameters are considered, it is evident that :

(1) the ratio J_2/k_1 is important in the thermosphere.

(2) the ratio k_2J_2/k_3J_3 is important in the stratosphere.

In the mesosphere all parameters are involved, since the day-time equilibrium conditions are :

$$\frac{n(O_3)}{n(O)} = \frac{k_2 \, n(M) \, n(O_2) - k_3 \, n(O_3)}{J_3} \tag{26}$$

and

$$n^2(O) \, k_1 n(M) \left[1 + \frac{k_3 \, k_2 \, n(O_2)}{k_1 \left\{ J_3 + k_3 \, n(O) \right\}} \right] = n(O_2) J_2 \tag{27}$$

in which the terms $k_3 \, n(X)$ can be neglected.

If there is no theoretical obstacle in discussing the ozone-atomic oxygen problem, numerical results differ by a large factor. The difficulties mentioned concerning the photodissociation rate coefficients are not important compared with the inaccuracies in the chemical rate coefficients. The rate coefficient of the three-body reaction (13) of oxygen atoms [14] can be taken as aeronomic purposes

$$k_1 = (3 \pm 1) \times 10^{-33} \, cm^6 \, sec^{-1} \tag{28a}$$

corresponding to the values assumed by Bates - Nicolet[4]

$$k_3 = 5 \times 10^{-34} \, T^{1/2} \, cm^6 \, sec^{-1} . \tag{28b}$$

The values of k_2 and k_3 are not yet certain. Using the laboratory values of Eucken and Patat[24], Bates and Nicolet[4] adopted

$$k_2 = 5 \times 10^{-36} \, T^{1/2} \, cm^6 \, sec^{-1} \tag{29}$$

and $\quad k_3 = 1.5 \times 10^{-11} \, T^{1/2} \, e^{-3000/T} \, cm^3 \, sec^{-1} . \tag{30}$

However, recent investigations such as Benson and Axworthy [25], Zaslowsky[26] and Kaufman[27] lead to

$$k_2 = (5 \pm 2.5) \times 10^{-34} \, cm^6 \, sec^{-1} \tag{31}$$

with an undetermined activation energy.

As regards the value of k_3, an exact evaluation is difficult [15]. The uncertainty is illustrated by the values deduced from laboratory measurements, namely[15]

$$k_{3a} = 5 \times 10^{-11} e^{-3000/T} \; cm^3 \; sec^{-1} \tag{32a}$$

and

$$k_{3b} = 7 \times 10^{-12} e^{-1600/T} \; cm^3 \; sec^{-1} \tag{32b}$$

If H_2O is an impurity in the measurement, k_{3b} could be the result of the bimolecular reaction between ozone and atomic hydrogen and k_{3a} should be the exact rate coefficient. It is clear that only approximate numerical solutions can be derived as the uncertainties in the coefficients are too great. The results obtained with (28a), (31) and (32a) or (32b) are given in Fig. 4 and exhibit the same general features found by earlier workers. But the absolute values are essentially different. An activation energy of 6 kcal for the bimolecular process $O_3 + O$ with a relatively small ratio $k_1/k_2 \leq 6$ leads to large concentrations of ozone and atomic oxygen in the mesosphere. Also the limit set for night-time conditions by

$$n(O_3)_{limit} = \frac{k_2}{k_3} \; n(M) \; n(O_2) \tag{33}$$

or by

$$n(O_3)_{limit} = n(O)_{DAY} \tag{34}$$

leads to an ozone concentration in the mesosphere much larger at night than during the day for k_{3b}. Consequently, there is a need for careful experimental work on ozone reactions. It must be stressed that extremely precise data are required for the analysis of aeronomic conditions in the mesosphere, in which it is possible to study photochemical and chemical processes without additional effects such as advective and dynamical transport and without a practical influence of solar activity. Without a perfect knowledge of the ozone - atomic oxygen behavior in a pure oxygen mesosphere it becomes difficult to study departures from photochemical equilibrium conditions in the stratosphere and thermosphere. Finally, the introduction of other minor constituents necessary in the study of the terrestrial atmosphere cannot be made if the idealized
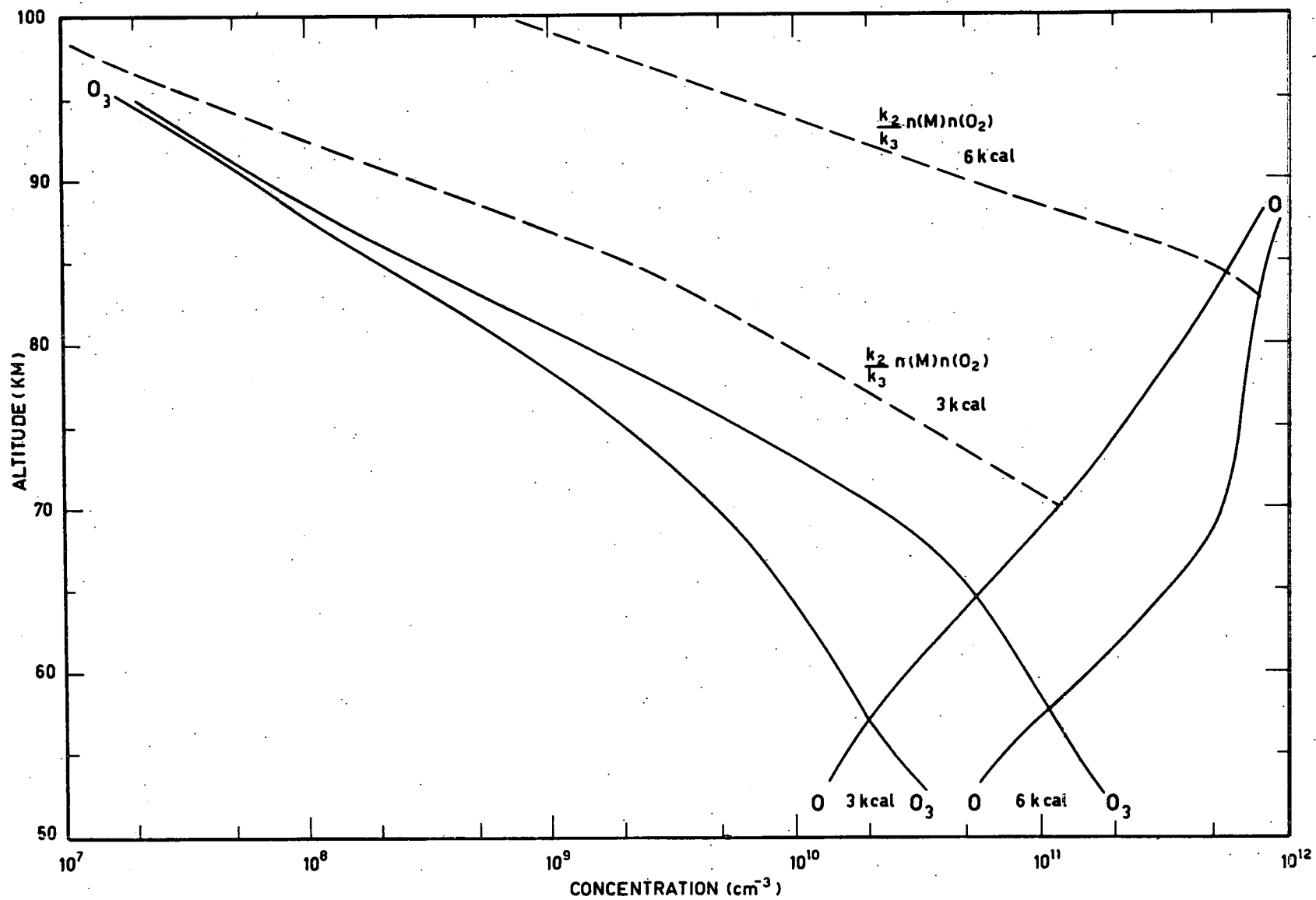
FIGURE 4.

16.

atmosphere is not properly defined.

4.- Origin of a hydrogen - oxygen atmosphere.

A hydrogen-oxygen atmosphere is very complicated. Photoaction on water vapor in the mesosphere and oxidation of methane in the stratosphere are important processes leading to the production of hydrogen atoms[7, 8]. Bates and Nicolet [4] made the first attempt to estimate the various aeronomic processes thirteen years ago and are now again considering (with the new experimental data [16]) the very complicated situation resulting from chemical actions and atmospheric mixing effects.

It has been shown[28] that there is a continuous escape of atomic hydrogen atoms at exospheric levels corresponding to a diffusion flow $F_D(H)$ at the 100 km level of the order of

$$F_D(H)_{100 \text{ km}} = 2.5 \times 10^7 \text{ cm}^{-2}\text{sec}^{-1} . \tag{35}$$

This must correspond to a total loss of about 10^7 H_2O molecules $cm^{-2}sec^{-1}$ or 6×10^6 CH_4 molecules $cm^{-2}sec^{-1}$. Under mixing conditions, the diffusion flow [29] of methane with concentration $n(CH_4) = 1.5 \times 10^{-6} n(M)$ is

$$F_D(CH_4) = 7 \times 10^6 \text{ cm}^{-2}\text{sec}^{-1} \tag{36}$$

which must be compared with a production rate [9] of CH_4 of at least 10^{10} molecules $cm^{-2}sec^{-1}$. Thus, the escape flow is always supported by the diffusion flow of CH_4 and is a small fraction of its total production.

Atomic oxygen attacks methane through

$$CH_4 + O \rightarrow CH_2 + H_2O + 30 \text{ kcal} \tag{37}$$
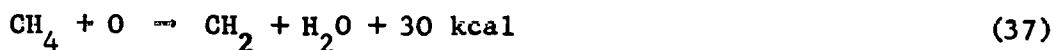
with an activation energy of the order of 7-8 kcal[30, 31]. Adopting

$$a(CH_4, O) = 2 \times 10^{-11} e^{-4000/T} = 4 \times 10^{-12} e^{-3600/T} \text{ cm}^3\text{sec}^{-1} \tag{38}$$

for the rate coefficient of (37), it appears that the life-time of CH_4 in the

mesosphere is relatively short[8]. As the re-formation of CH_4 is a very slow process, its concentration in the mesosphere must be very small. There is no diffusion or atmospheric mixing process able to maintain an adequate vertical flow of methane. It is almost certain that its fractional abundance begins to fall off well below the stratopause. With a rate coefficient of the order of 10^{-19} $cm^3 sec^{-1}$ for (37), adapted to tropopause conditions corresponding to about 5×10^{12} CH_4 molecules cm^{-3}, it can be seen that a 10 km layer with about 10^7 oxygen atoms cm^{-3} will lead to a production of about 10^7 H_2O molecules $cm^{-2} sec^{-1}$. Judging from this value it seems probable that, in the stratosphere, the fractional concentration of CH_4 is affected by its transformation into H_2O, and consequently the formation of H_2O depends on the methane exchange between the troposphere and the stratosphere. The tropospheric mixing time is short enough to lead to a uniform vertical distribution of CH_4[32], and its injection rate into the stratosphere should be known with precision in order to determine the actual production of stratospheric H_2O. With uniform transport due to diffusion, its fractional abundance would be about 3×10^{-6}. However, since the life-times $\tau(CH_4)$ at 30 km and 40 km are of the order

$$\tau(CH_4)_{40 \text{ km}} = 1 \text{ year} \tag{39}$$

and

$$\tau(CH_4)_{30 \text{ km}} = 10 \text{ years}, \tag{40}$$

this implies that the exchange between troposphere and stratosphere is controlled by "turbulent" processes rather than by diffusion. Consequently, an abundance of H_2O greater than 3×10^{-6} can result from methane oxidation in the stratosphere.

5.- Reactions of atomic hydrogen.

The products of dissociation of H_2O in the mesosphere give rise to a complicated series of chemical processes. More than 30 processes are involved[4] and we retain here the more important processes that a detailed study of the situation suggests. The principal reactions are listed below.

Those involving hydrogen atoms are :

$$H + O_2 + M \rightarrow HO_2 + M + 46 \text{ kcal}, \tag{41}$$
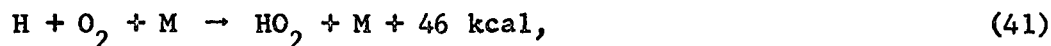
with a rate coefficient according to Clyne and Trush[33]

$$a_1 = 1.3 \times 10^{-33} e^{800/T} \text{ cm}^6 \text{sec}^{-1} \tag{42}$$

showing a negative temperature coefficient, and

$$H + O_3 \rightarrow OH + O_2 + 77 \text{ kcal} \tag{43}$$

for which the rate coefficient a_2[16] is very large,

$$a_2 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1}. \tag{44}$$

This reaction was introduced by Bates-Nicolet[4] in 1950 to explain the observed airglow emission of the hydroxyl radicle OH up to the vibrational quantum number 9 (75.2 kcal) but not up to $v'' = 10$ (81 kcal).

The same reaction, leading to HO_2, is less important and instead of the three-body association between OH and O, the bimolecular process

$$OH + O \rightarrow H + O_2 + 16.6 \text{ kcal} \tag{45}$$

is noted as also having a high rate coefficient with practically no activation energy[16]

$$a_5 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1} \tag{46}$$

Since $O_2(X^3\Sigma_g^-)_{v = 4} = 17.4$ kcal only the first 3 vibrational levels of O_2 are involved.

The reaction of HO_2 with O is also a fast process [16]

$$HO_2 + O \rightarrow OH + O_2 + 55 \text{ kcal} \tag{47}$$

with a rate coefficient a_7 which may reach

$$a_7 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1}. \tag{48}$$

Assuming as a first approximation that only the preceding reactions are involved, the following ratios corresponding to chemical equilibrium conditions are obtained :

$$\frac{n(OH)}{n(H)} = \frac{a_1 \, n(M) \, n(O_2) + a_2 \, n(O_3)}{a_5 \, n(O)} \qquad (49)$$

and

$$\frac{n(HO_2)}{n(H)} = \frac{a_1 \, n(M) \, n(O_2)}{a_7 \, n(O)} . \qquad (50)$$

Since atomic oxygen is present in the mesosphere with concentrations not less than 10^{10} cm^{-3} during the day, (49) and (50) are representative of day-time conditions.

At the stratopause level $a_1 \, n(M) \, n(O_2) \simeq 5$ sec^{-1} is the most important term in equations (49) and (50), and, therefore, $n(HO_2) > n(H)$ and $n(CH) > n(H)$. Atomic hydrogen becomes important only in the mesosphere (and above). The rapid decrease of the term $a_1 \, n(M) \, n(O_2)$ with height compared with that of bimolecular processes leads to the approximation, somewhere above the stratopause,

$$\frac{n(OH)}{n(H)} = \frac{1}{2} \frac{n(O_3)}{n(O)} . \qquad (51)$$

This indicates, since $n(O_3) < n(O)$ in the middle mesosphere and thermosphere, that the hydroxyl radicle OH must have an upward sharp decline. Under the same conditions, i.e. $a_2 \, n(O_3) > a_1 \, n(M) \, n(O_2)$, we have $n(OH) > n(HO_2)$, which indicates that hydrogen is in atomic form to such a degree as to play an important role in mesospheric processes.

If atomic hydrogen is sufficiently abundant in the mesosphere, equation (20) must be modified by adding another term,

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1 \, n(M) \, n^2(O) + 2k_3 \, n(O_3) \, n(O)$$

$$+ 2 \, a_2 \, n(O_3) \, n(H) = 2 \, n(O_2) \, J_2 \quad . \tag{52}$$

Again, in order to derive any numerical value, it is necessary to know first the exact numerical expressions in a pure oxygen atmosphere. In any case, comparing the numerical values of k_3 and a_2, it is clear that for atomic hydrogen concentrations in the mesosphere greater than $10^7 \, cm^{-3}$

$$k_3 \, n(O) < a_2 \, n(H) \quad . \tag{53}$$

Since $n(H)$ is of the order of $10^7 \, cm^{-3}$ at 100 km [28, 34] and increases downwards in the lower thermosphere, it is certain that the ozone-oxygen equilibrium in the mesosphere is affected by atomic hydrogen which acts as a catylist.

As a example, let's assume a concentration of $n(H) = 3 \times 10^8 \, cm^{-3}$ at 80 km, namely a normal value if atomic hydrogen is in mixing between 80 km and 100 km. The ozone concentration which is about $10^9 \, cm^{-3}$ in a pure oxygen atmosphere (see Fig. 4) decreases to $10^8 \, cm^{-3}$ and the atomic oxygen concentration decreases from $7 \times 10^{11} \, cm^{-3}$ to $10^{11} \, cm^{-3}$. It is clear, therefore, that the mesospheric behavior of a hydrogen-oxygen atmosphere is completely different from a pure oxygen atmosphere.

6.- Reactions in a hydrogen-oxygen atmosphere.

Numerous secondary processes, involving the destruction of atomic hydrogen, hydroxyl and perhydroxyl radicles occur in the mesosphere. Among the data required for a complete discussion are the rate coefficients of the various reactions of all hydrogen - oxygen compounds [16]. Recent publications on the subject were also used as main sources [35, 36, 37, 38] since a number of investigators have studied these reactions under various aspects.

The source of hydrogen atoms (free or combined) is the photodissociation of H_2O (and H_2O_2). The final loss processes which are directly related to

hydrogen atoms are not important compared with collision processes where OH and HO_2 are involved. This is due to the fact that at the stratopause and in the lower mesosphere $n(H) < n(OH) < n(HO_2)$ and also that the reactions are not very rapid. The main final reactions are as follows :

Between two hydroxyl radicles,

$$OH + OH \rightarrow H_2O + O + 17 \text{ kcal}, \tag{54}$$

which is discussed by Kaufman [16] and has a reaction rate

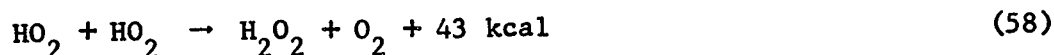$$a_{16} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{sec}^{-1} . \tag{55}$$

Between hydroxyl and perhydroxyl radicles,

$$OH + HO_2 \rightarrow H_2O + O_2 + 72 \text{ kcal} \tag{56}$$

for which a high rate coefficient is suggested [16] and is taken as

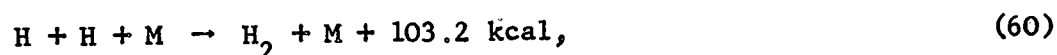$$a_{17} = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1} . \tag{57}$$

Between two perhydroxyl radicles

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 + 43 \text{ kcal} \tag{58}$$

with a rate coefficient of the same order as a_{16}, i.e.

$$a_{27} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1} . \tag{59}$$

Among the loss processes of atomic hydrogen which could be added to the reactions just described, we may consider the three-body reactions :

$$H + H + M \rightarrow H_2 + M + 103.2 \text{ kcal}, \tag{60}$$

with rate coefficient a_{21} of the order

$$a_{21} = 3 \times 10^{-32} \text{ cm}^6 \text{sec}^{-1} \tag{61}$$

The exothermic bimolecular process

$$H + OH \rightarrow H_2 + O + 1.9 \text{ kcal} \tag{62}$$

with rate coefficient

$$a_{22} = 2 \times 10^{-13} \ T^{1/2} \ e^{-3400/T} \ \text{cm}^3 \text{sec}^{-1} \tag{63}$$
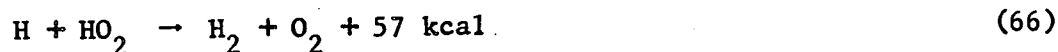
can be compared with the endothermic process

$$H_2 + O \rightarrow OH + H - 1.9 \text{ kcal} \tag{64}$$
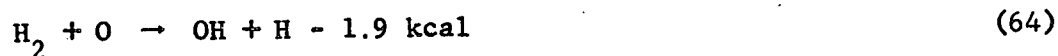
with rate coefficient

$$a_{24} = 5 \times 10^{-13} \ T^{1/2} \ e^{-4400/T} \ \text{cm}^3 \text{sec}^{-1}. \tag{65}$$

Such a process is important in the thermosphere since it leads to the final dissociation of molecular hydrogen.

Finally, the reaction with perhydroxyl radicles

$$H + HO_2 \rightarrow H_2 + O_2 + 57 \text{ kcal} \tag{66}$$

with a rate coefficient

$$a_{23} = 5 \times 10^{-12} \ T^{1/2} \ e^{-1000/T} \ \text{cm}^3 \text{sec}^{-1} \tag{67}$$

should be a normal production process of molecular hydrogen.

The expression for complete equilibrium is written as follows :

$$n(H_2O) \ J_{H_2O} + n(H_2O_2) \ J_{H_2O_2} + a_{24} \ n(O) \ n(H_2) =$$

$$a_{16} \ n^2(OH) + a_{17} \ n(OH) \ n(HO_2) + a_{27} \ n^2(HO_2)$$

$$+ a_{21} \ n(M) \ n^2(H) + a_{22} \ n(H) \ n(OH) + a_{23} \ n(H) \ n(HO_2) \tag{68}$$

which can be applied in the mesosphere for daytime conditions.

The vertical distribution of the production function depends

on the values of $n(H_2O)$ and J_{H_2O} for which exact values are not available. Because of absorption due to molecular oxygen, J_{H_2O} is a very sensitive function of the optical depth of molecular oxygen. Various estimates can be made, but it is not possible to discuss here all aspects which must be considered for a complete discussion.

The omission of reactions involving atomic hydrogen at sufficiently low altitudes (above the stratopause) where $n(H)$ must decrease rapidly according to (49) leads to a simple way of considering the result of night-time conditions. The differential equation is simply, see (68),

$$- \left[\frac{dn(OH)}{dt} + \frac{d(HO_2)}{dt} \right] = a_{16} \, n^2(OH) + a_{27} \, n^2(HO_2) + a_{17} \, n(OH) \, n(HO_2) \quad (69)$$

Since (55), (57) and (58) show that $a_{16} = a_{27} \leqslant \frac{1}{2} \, a_{17}$, the relevant solution to (69) is simply, t being the time measured from t_o which is sunset,

$$n_t(OH) + n_t(HO_2) \leqslant 1 \left/ \left\{ \frac{1}{n_{t_o}(OH) + n_{t_o}(HO_2)} + a_{16} \, t \right\} \right. \quad (70)$$

The nocturnal decay is important in the lower mesosphere since for $a_{16} = 2.5 \times 10^{-12}$ $cm^3 sec^{-1}$ and $t = 4 \times 10^4 sec$ the initial concentration is reduced to less $10^7 cm^{-3}$.

Thus, even if the aeronomic problem considered in this section is idealized, it does indicate that the whole mesosphere is a transition region in which the free hydrogen atoms are formed and diffuse upwards. Water vapor diffuses from the stratosphere into the dissociation region with an equivalent current which can be furnished by methane in the troposphere. If gentle mixing winds occur and carry up H_2O, at a greater rate, then there will be regions of abnormal specific humidity which will persist for a certain period of time. But the final process must be a downward transport of water vapor.
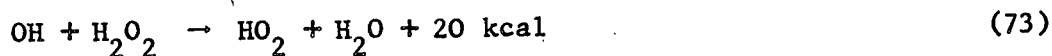
The reactions (54), (56) and (58) obviously lead to H_2O since hydrogen peroxide is destroyed (see for example references [35, 39, 40]) by the following

chemical processes :

$$H + H_2O_2 \rightarrow OH + H_2O + 59 \text{ kcal} \tag{71}$$
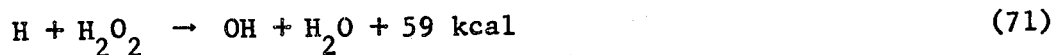
with a rate coefficient of the order

$$a_{29} = 1.5 \times 10^{-13} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{sec}^{-1}, \tag{72}$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O + 20 \text{ kcal} \tag{73}$$

with a rate coefficient which may be

$$a_{30} = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1} \tag{74}$$

and

$$O + H_2O_2 \rightarrow O_2 + H_2O + 75 \text{ kcal} \tag{75}$$

with a rate coefficient

$$a_{31} = 3 \times 10^{-13} T^{1/2} e^{-2000/T} \text{ cm}^3 \text{sec}^{-1} \tag{76}$$

The exact role of hydrogen peroxide near the stratopause level must be redetermined from the solution of the differential equation

$$\frac{dn(H_2O_2)}{dt} + n(H_2O_2) \left[J_{H_2O_2} + a_{29} n(H) + a_{30} n(OH) + a_{31} n(O) \right]$$

$$= 2 a_{27} n^2(HO_2) \tag{77}$$

An approximate value for $J_{H_2O_2}$ is 10^{-4} sec^{-1}, and almost equilibrium day-time conditions can be imposed.

Molecular hydrogen should exist in the mesosphere since its dissociation probability is small in this region. In addition to processes (62) and (67) leading to the formation of H_2, and to (65) leading to the loss

of H_2, we may consider also

$$OH + H_2 \rightarrow H_2O + H + 15 \text{ kcal} \tag{78a}$$

with a rate coefficient a_{19} of the order of

$$a_{19} = 5 \times 10^{-12} \ T^{1/2} \ e^{-3000/T} \ . \tag{78b}$$

The general equation being

$$\frac{dn(H_2)}{dt} + n(H_2) \left[a_{24} \ n(O) + a_{19} \ n(OH) \right] = n(H) \left[a_{22} \ n(OH) + a_{23} \ n(HO_2) \right] . \tag{79}$$

This leads only to equilibrium conditions when $a_{24} \ n(O)$ is sufficiently large, i.e. in the thermosphere where the temperature is high.
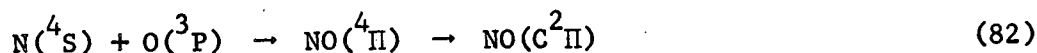
7.- Nitrogen dioxide.

If nitrogen dissociation is operative at sufficiently low altitudes, the formation of nitric oxide may be due to a three-body process
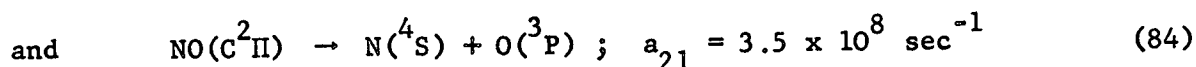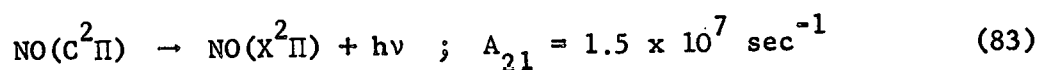
$$N + O + M \rightarrow NO + M + 150 \text{ kcal} \tag{80}$$
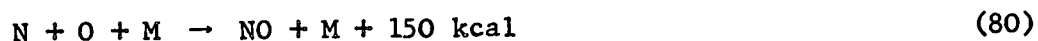
for which the rate coefficient b_o is of the order[41]

$$b_o = 5 \times 10^{-33} \ cm^6 \ sec^{-1} \tag{81}$$

A pre-association process such as [42, 43]

$$N(^4S) + O(^3P) \rightarrow NO(^4\Pi) \rightarrow NO(C^2\Pi) \tag{82}$$

followed by

$$NO(C^2\Pi) \rightarrow NO(X^2\Pi) + h\nu \ ; \ A_{21} = 1.5 \times 10^7 \ sec^{-1} \tag{83}$$

and $$NO(C^2\Pi) \rightarrow N(^4S) + O(^3P) \ ; \ a_{21} = 3.5 \times 10^8 \ sec^{-1} \tag{84}$$

leads to nitric oxide formation with a rate coefficient

$$b_1 = 1 \times 10^{-17} cm^3 \ sec^{-1} \tag{85}$$

which is more effective than (81) where n(M) is less than $10^{15} \ cm^{-3}$, i.e. near 75 km.

Before studying other processes leading to the formation of nitric oxide, it is necessary to simplify the study of nitric oxide by considering its reactions with atomic oxygen and ozone.
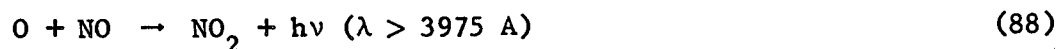
First, the following three-body process

$$O + NO + M \rightarrow NO_2 + M + 71 \ kcal \tag{86}$$
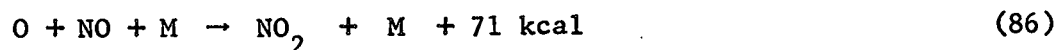
having a rate coefficient [44] given by

$$b_{2a} = 3 \times 10^{-33} \ e^{1000/T} \ cm^6 \ sec^{-1} \tag{87}$$

must be compared with the radiative process with pressure above 0.1 Torr

$$O + NO \rightarrow NO_2 + h\nu \ (\lambda > 3975 \ A) \tag{88}$$

with a rate coefficient [15] ($\lambda\lambda$ 3875 A - 1.4μ)

$$b_{2b} = 6.4 \times 10^{-17} \ cm^3 sec^{-1} \tag{89}$$

with for $\lambda < 6200$ A, $b_{2b} = 1.5 \times 10^{-17} \ cm^3 sec^{-1}$ (90)

Two bimolecular processes must be considered as important aeronomic reactions. One is a reaction with oxygen atoms

$$O + NO_2 \rightarrow NO + O_2 + 46 \ kcal \tag{91}$$

with a high rate coefficient for vibrational excitation [45, 46] of O_2 up to v" = 8 (33.7 kcal), and perhaps also for an electronic excitation to $^1\Sigma g$ (v' $\geq$ 0, $\geq$ 37.5 kcal) corresponding to v" $\geq$ 9,

$$b_3 = 5 \times 10^{-12} \, T^{1/2} \, e^{-1000/T} \, cm^3 sec^{-1} \; . \tag{92}$$

The other reaction is with ozone [47] and it leads to ground-state NO_2 molecules

$$O_3 + NO \rightarrow NO_2 + O_2 + 47 \; kcal \tag{93}$$
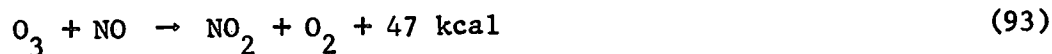
with a rate coefficient

$$b_4 = 5 \times 10^{-14} \, T^{1/2} \, e^{-1200/T} \, cm^3 sec^{-1} \tag{94}$$

The chemilunescent reaction at $\lambda > 5900$ A [48] resulting from electronically excited molecules would have an activation energy of 4.2 kcal [49].

In addition to these processes involving NO_2, the following photo-dissociation process occurs in a sunlit atmosphere :

$$NO_2 + h\nu \rightarrow NO + O \tag{95}$$

with the high rate coefficient [11]

$$J_{NO_2} \cong 5 \times 10^{-3} \, sec^{-1} \; . \tag{96}$$

Under laboratory conditions the photolysis of nitrogen dioxide must involve an analysis [50] of NO_3, N_2O_5 etc. However, if a reaction such as $O_3 + NO_2 \rightarrow NO_3 + O_2$ has an activation energy of the order of 7 kcal, NO_2 will not be affected during the night. For day time conditions excluding NO_3 aeronomic conditions essentially correspond to an approximation of the $NO - NO_2$ system.

Neglecting here reactions in which hydrogen and nitrogen atoms are involved, the differential equation related to NO_2 is written as

$$\frac{dn(NO_2)}{dt} + \left[b_3 \, n(O) + J_{NO_2} \right] n(NO_2) = \left[b_2 \, n(O) + b_4 \, n(O_3) \right] n(NO) \quad . \tag{97}$$

For daytime conditions, an equilibrium exists and

$$\frac{n(NO_2)}{n(NO)} = \frac{[b_{2a} \, n(M) + b_{2b}] \, n(O) + b_4 \, n(O_3)}{J_{NO_2} + b_3 \, n(O)} \tag{98}$$

Fig. 5 is an illustration of the vertical distribution of the ratio $n(NO_2)/n(NO)$ which shows that above the stratopause it is always possible to neglect the effect of nitrogen dioxide for photoequilibrium conditions.

After twilight, when atomic oxygen is rapidly removed in the stratosphere, the essential process is, according to (97),

$$\frac{dn(NO_2)}{dt} = - \frac{dn(NO)}{dt} = b_4 \, n(O_3) \, n(NO) . \tag{99}$$

The life-time of NO is very short during the night in the stratosphere since $b_4 \, n(O_3) > 3 \times 10^{-4} \sec^{-1}$ (see Fig. 5). In other words, nitric oxide disappears during dark hours in the atmospheric regions where ozone is present in sufficient numbers (reaction 93).

In the upper mesosphere and thermosphere where $n(O)$ does not vary appreciably, the differential equation (97) in which $J_{NO_2} = 0$ and $b_3 n(O) > b_4 n(O_3)$ indicates that the ratio $n(NO_2)/n(NO)$ increases after sunset as follows :

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2}{b_3} \left[1 - e^{-b_3 \, n(O) \, t} \right] \tag{100}$$

Night-time equilibrium conditions are reached very rapidly in the thermosphere but do not differ from daytime conditions (see Fig. 5). It can be seen from curves of Fig. 5 that the ratio $n(NO_2)/n(NO)$ varies in the middle mesosphere where it depends on the rapidly varying concentrations of O_3 and O after sunset.

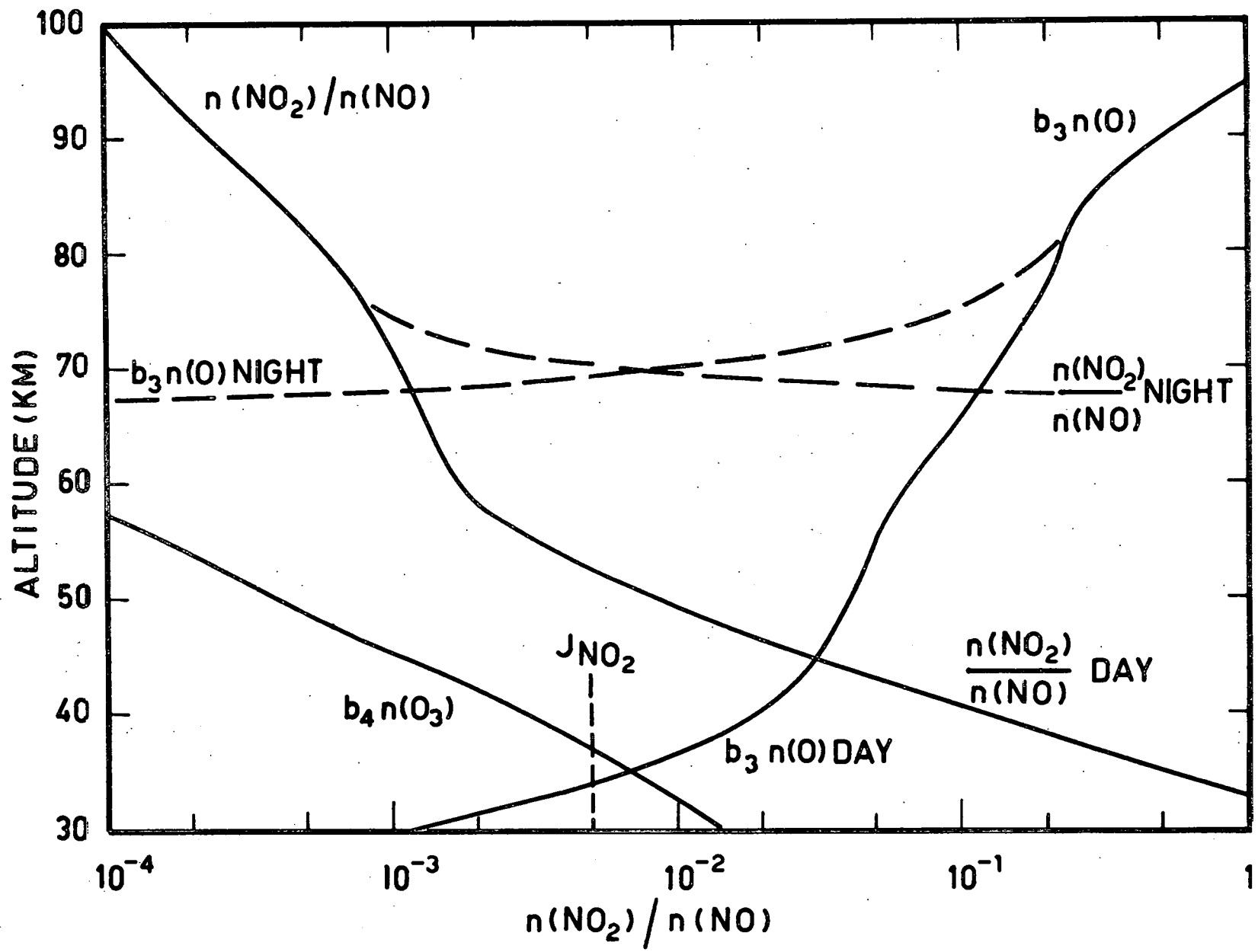Finally, it must be pointed out that in the stratosphere below 30 km

FIGURE 5.

where the photoaction plays a role the ratio $n(NO_2)/n(NO)$ increases leading to a greater NO_2 concentration than that of NO.

8.- Nitric oxide.

In order to determine the behavior of nitric oxide, it is necessary to determine aeronomic reactions in which atomic nitrogen is effectively involved. In addition to (80) and (82), nitrogen atoms can react with nitrogen dioxide

$$N + NO_2 \rightarrow NO + NO \quad \text{or} \quad O + N_2O \quad \text{or} \quad N_2 + O_2 \tag{101}$$
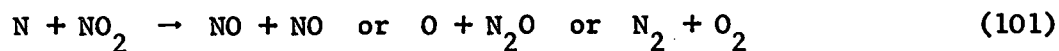
for which a rate coefficient b_5 may be of the order of other bimolecular reactions. However, the reaction of nitrogen atoms with nitric oxide is certainly more important (see discussions [15]) :

$$N + NO \rightarrow N_2 + O + 75 \text{ kcal} \tag{102}$$

with a rate coefficient such as

$$b_6 = 1.5 \times 10^{-12} T^{1/2} cm^3 sec^{-1} \tag{103}$$

having a negligible activation energy plays a leading role. The fact that vibrational excitation of N_2 $(v \leqslant 12)$ occurs in reaction (102) and decomposes O_3 is of no practical aeronomic consequence since it can be shown that reaction (102) is a thermospheric reaction and is without importance at mesospheric levels. The reaction is, however, the most important process leading to nitrogen recombination in the thermosphere.

With a full realization of all possible reactions of nitrogen atoms under aeronomic conditions, reactions with molecular oxygen and ozone must be added.

$$N + O_2 \rightarrow NO + O + 32 \text{ kcal}, \tag{104}$$

with maximum vibrational NO $(v = 6)$ excitation, requires a relatively high activation energy [51, 52, 53], between 6 and 7 kcal. Its rate coefficient

$$b_7 = 1.5 \times 10^{-13} \, e^{-3000/T} \, cm^3 sec^{-1} \qquad (105)$$

is small at low temperature ; nevertheless, it leads to an aeronomic rate coefficient of about 10^{-5} sec^{-1} at the mesopause level and about 10^{-3} sec^{-1} in the thermosphere.

Production of nitric oxide in the laboratory may also result from the reaction of nitrogen atoms with ozone [54, 55]

$$N + O_3 \rightarrow NO + O_2 + 126 \text{ kcal} \qquad (106)$$

having a rate coefficient of the order of

$$b_8 = 1.5 \times 10^{-12} \, T^{1/2} \, e^{-1200/T} \, cm^3 \, sec^{-1} . \qquad (107)$$

This reaction could have an aeronomic role (only in the mesosphere) if nitrogen atoms were present. In fact this reaction can be neglected since nitrogen atoms are not available at these atmospheric levels.

In addition to the loss process (102) of nitric oxide occuring in day and night-time conditions, it is necessary to add the following photo-dissociation process.

$$NO + h\nu \, (\lambda \sim 1900 \text{ A}) \rightarrow N + O \qquad (108)$$

for which Bates[11] has adopted a rate coefficient at zero optical depth

$$J_{NO} = 10^{-7} \, sec^{-1}.$$

Furthermore, the photoionization of NO by Lyman-alpha followed by dissociative recombination is also a loss process :

$$NO + h\nu \, (\lambda \, 1216 \text{ A}) \rightarrow NO^+ + e \rightarrow N + O . \qquad (109)$$
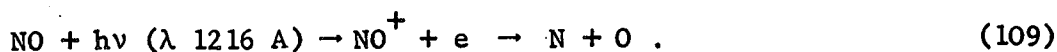
An average value of about 4 ergs cm^{-2}sec^{-1} for solar Ly-α leads to a rate coefficient at zero optical depth of

$$I_{NO} = 5 \times 10^{-7} \, sec^{-1} \qquad (110)$$

With equilibrium conditions between nitrogen dioxide and nitric oxide, the rate of change of $n(NO)$ is given by the following equation :

$$\frac{dn(NO)}{dt} + n(NO) \left[I_{NO} + J_{NO} + b_6 \, n(N) \right] = \left[b_1 \, n(NO) + b_7 \, n(O_2) \right] n(N) \qquad (111)$$

Hence, writing $dn(NO)/dt = 0$ in (111), the ratio $n(NO)/n(N)$ is given by

$$\frac{n(NO)}{n(N)} = \frac{b_1 \, n(O) + b_7 \, n(O_2)}{I_{NO} + J_{NO} + b_6 n(N)} . \qquad (112)$$

In this formula, $b_6 \, n(N)$ is the important term in the denominator if $n(N) > 5 \times 10^4 \, cm^{-3}$. If we ignore I_{NO} and J_{NO}, the equilibrium value of nitric oxide $n^*(NO)$ is

$$n^*(NO) = 10^{-1} \, e^{-3000/T} \, n(O_2) + 5 \times 10^{-7} \, n(O) \qquad (113)$$

Here the second term on the right is small compared to the first one in the mesosphere and lower regions. It is important only at the atomic oxygen density peak which occurs in the lower thermosphere, since it becomes negligible where the temperature is high in the thermosphere. A concentration of oxygen atoms of the order of $2 \times 10^{12} \, cm^{-3}$ leads to

$$n^*(NO) = 10^6 \, cm^{-3} . \qquad (114)$$

At the mesopause level, equation (113) leads to

$$n^*(NO) = 5.6 \times 10^5 \, cm^{-3} \qquad (115)$$

i.e. 3×10^{-9} of the total concentration.

The time to reach an equilibrium according to (111) depends on the term $b_6 \, n(N)$ and if $n(N) > n(NO)$, all conditions are required to reach a perfect chemical equilibrium. At the mesopause level an atomic nitrogen concentration

of at least of 10^6 cm^{-3} is required to apply strictly equilibrium conditions, which can be reached in less than one day. Consequently, the production of nitrogen atoms must be studied near the mesopause level before deducing the aeronomic behavior of nitric oxide.

If we write $I_{NO} + J_{NO} > b_6 \, n(N)$, so that (112) becomes

$$\frac{n(NO)}{n(N)} = \frac{b_7 \, n(O_2)}{I_{NO} + J_{NO}} \qquad (116)$$

applicable to mesospheric conditions, we get a ratio $n(NO)/n(N)$ greater than unity and increasing downwards.

9.- Atomic Nitrogen.

Using the set of reactions written above, the equation governing the rate of change of atomic nitrogen is

$$\frac{dn(N)}{dt} + n(N) \left[b_1 \, n(O) + b_6 \, n(NO) + b_7 \, n(O_2) \right] = n(NO) \left[J_{NO} + I_{NO} \right] + 2P(N) \qquad (117)$$

in which the last term on the right takes into account various possibilities of atomic nitrogen production.

In the chemosphere, only the following predissociation process considered by Herzberg [56] can be introduced :

$$N_2 + h\nu \; (\lambda\lambda \sim 1200 \; \text{to} \; 1250A) \rightarrow N_2(a\,^1\Pi_g) \rightarrow N + N \qquad (118)$$
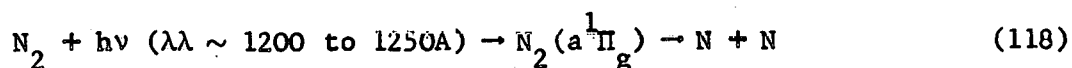
in which Lyman-Birge-Hopfield bands are involved, namely (7-0) at 1250 A, (8-0) at 1226A and (9-0) at 1205A. The most penetrating radiation corresponds to 1226A for which the absorption cross-section should be of the order of 5×10^{-19} cm^2. According to Bates [11] an approximate value of the dissociation rate coefficient at zero optical depth should be about

$$J_{N_2} = 10^{-12} \ sec^{-1} \ . \tag{119}$$

Other processes leading to the production of nitrogen atoms must deal with ionospheric processes which have been discussed by Dalgarno at this meeting. An important ion-atom interchange reaction is

$$O^+ + N_2 \rightarrow NO^+ + N + 25 kcal \tag{120}$$

leading to vibrationally excited NO^+ molecules up to $v" = 3$. It is more important than the dissociative recombination of N_2^+ since the charge transfer processes $O_2 + N_2^+ \rightarrow O_2^+ + N_2$ and $O + N_2^+ \rightarrow O^+ + N_2$ play a leading role in eliminating N_2^+ in the ionospheric layers. In addition, the following ion-atom interchange reaction

$$O_2^+ + N_2 \rightarrow NO^+ + NO + 22 \ kcal \tag{121}$$

cannot be rejected in the lower ionosphere even if its activation energy is very large.

Considering the ionospheric and chemospheric processes which are involved in the production of nitrogen atoms it is clear first that ionospheric production is the most important process in the F layers for daytime conditions and leads to photoequilibrium conditions. In the lower thermosphere, the chemospheric process (118) easily leads to a production of at least of 10 N atoms $cm^{-3} sec^{-1}$ while the ionospheric process is due to X-rays subject to large variations with solar activity. A production of 10 atoms $cm^{-3} \ sec^{-1}$ can be taken as merely illustrative of a possible production near the mesopause level.

By adding (111) and (117), we obtain the proper expression for photo-chemical changes

$$\frac{1}{2} d \left[n(NO) + n(N) \right] / dt + b_6 \ n(NO) \ n(N) = P(N) \tag{122}$$

which above the mesopause level can be used in the steady state to get a mean

value of $n(N)$

$$b_6 \, n(NO) \, n(N) = P(N) \tag{123}$$

For example, a round figure of $n(NO)$ being 10^6 $cm^{-3} sec^{-1}$ near 100 km leads to $n(N) \geqq 10^6$ cm^{-3}.

If we adopt the relations :

$$n^*(NO) = \frac{b_1 \, n(O) + b_7 \, n(O_2)}{b_6} \tag{124}$$

$$n^*(N_2) = \frac{P(N)}{b_1 \, n(O) + b_7 \, n(O_2)} \tag{125}$$

solutions of (123), the actual value of $n(NO)$ is

$$n(NO) = n^*(NO) \, / \, [1 + 10^5 / \, n^* \, (N)]^{1/2} \tag{126}$$

At the mesopause level, the term $b_7 \, n(O_2)$ is about 10^{-5} sec^{-1} and any production of nitrogen atoms greater than 1 atom $cm^{-3} sec^{-1}$ leads to a stationary value $n(NO)$ which is practically the equilibrium value $n^*(NO)$.

10.- Nitrogen dioxide and nitric oxide concentrations.

In the mesosphere, the loss of nitrogen atoms increases rapidly with decreasing height and equilibrium conditions can be always applied to atomic nitrogen. Thus we have, for the change of $n(NO)$ in the mesosphere, assuming that only chemical changes occur without convective transport

$$\frac{dn(NO)}{dt} + 2b_6 \, n^2(NO) \, \frac{I_{NO} + J_{NO}}{b_7 n(O_2) + b_6 n(NO)} =$$

$$2P(N) \left[\frac{b_7 \, n(O_2) - b_6 \, n(NO)}{b_7 \, n(O_2) + b_6 \, n(NO)} \right] \tag{127}$$

Since b_7 $n(O_2)$ must be greater than b_6 $n(NO)$, (126), and the atomic nitrogen concentration is very small, the following approximation can be applied :

$$- \frac{dn(NO)}{dt} = 2b_6 \frac{I_{NO} + J_{NO}}{b_7 \, n(O_2)} \, n^2(NO) \; . \tag{128}$$

Integrating (128), we obtain the life-time of nitric oxide in the mesosphere and the lower atmospheric regions. At the mesopause level, the time τ_{NO} necessary to reduce $n(NO)$ to 50 percent of its photochemical value is about 15 days. Now the general form of equation (128) shows that the trend of τ_{NO} is to increase as the altitude decreased. This obviously adds greatly to the possibility of maintaining nitric oxide in the mesosphere by atmospheric mixing.

Adopting an equilibrium value for nitric oxide at the mesopause level, i.e. a concentration $n^*(N) \geq 10^5$ cm^{-3} (equation 126) corresponding to a production of at least 2 nitrogen atoms $cm^{-3} sec^{-1}$ (equation 125), there is a possibility of making a calibration for the whole atmosphere. Using the same atmospheric parameters which have been adopted for the aeronomic study of ozone, we can write, (115),

$$n(NO) = 3 \times 10^{-9} \, n(M) \tag{129}$$

at 85 km with T = 190°K.

Below the mesopause, assuming a vertical distribution following the normal hydrostatic distribution, it is possible to deduce the life-times of nitric oxide. Illustrative figures for τ_{NO} are as follows :

80 km	1 month	70 km	6 months
75 km	3 months	65 km	2 years

Such a loss of nitric oxide below 65 km can be easily replaced by diffusion since it requires only about a flow of 3×10^4 NO molecules $cm^{-2} sec^{-1}$. In other words if a hydrostatic distribution is established in the lower mesosphere it can be easily maintained throughout the stratosphere by a diffusion

process. In the upper troposphere, i.e. at 75 km, it is no problem for diffusion to maintain at least 30 °/$_o$ of a NO concentration following the hydrostatic distributions. Assuming that a convective transport is not absent in the mesosphere, there is, therefore, no difficulty in assuming that the normal trend exhibited by nitric oxide below the mesopause is that following a hydrostatic distribution. Nevertheless, times of the order of 15-30 days are of significance in connection with the investigation of abnormal concentrations of nitric oxide near the mesopause level. Any variation in the production of nitrogen atoms in the mesosphere (solar flares, corpuscular radiation) or in the equilibrium conditions (variation of temperature) will affect the nitric oxide concentration for several days.

The photochemical value of $n(NO) = 3 \times 10^{-9} n(M)$ with its extrapolation into the mesosphere, stratosphere and troposphere leads to an acceptable concentration of nitrogen oxide at ground level[9, 56]. Considering the various ratios $n(NO_2)/n(NO)$ as obtained by (98) and (100) and shown in Fig. 5, it is possible to illustrate the vertical distributions of $n(NO)$ and $n(NO_2)$. Fig. 6 and Fig. 7 show the variation in the stratosphere and mesosphere, respectively. Nitrogen dioxide and nitric oxide have the same importance in the middle stratosphere around 30 km, and during the night, NO disapears by its transformation into NO_2. In the mesosphere there is a large variation between day and night. There is a transition zone corresponding to the region where atomic oxygen recombines after sunset. Above the mesopause, NO again increases and reaches a concentration peak of not less than 10^7 cm^{-3} around 150 km in the thermosphere. But its concentration in the E layer is only about 10^6 cm^{-3}. Nevertheless so much of the basic data is lacking that it would be unrealistic to consider the given figures as final. The uncertainties in the experimental data are too serious to allow the calculated distributions to be correct.

11.- Hydrogen and nitric oxide.

In a hydrogen-oxygen atmosphere, there are still other possible reactions involving a single hydrogen atom (free or conbined) and nitrogen oxides.
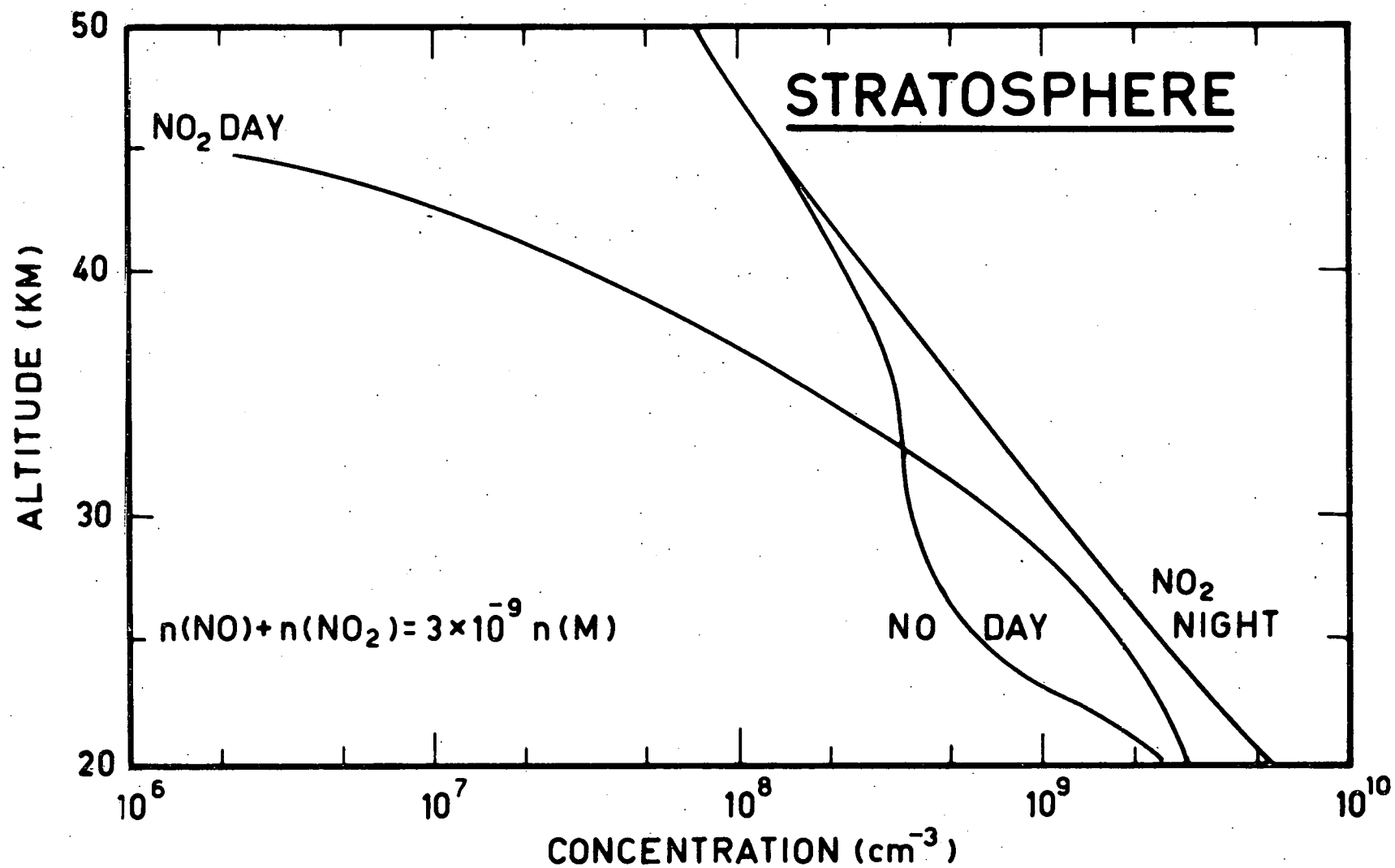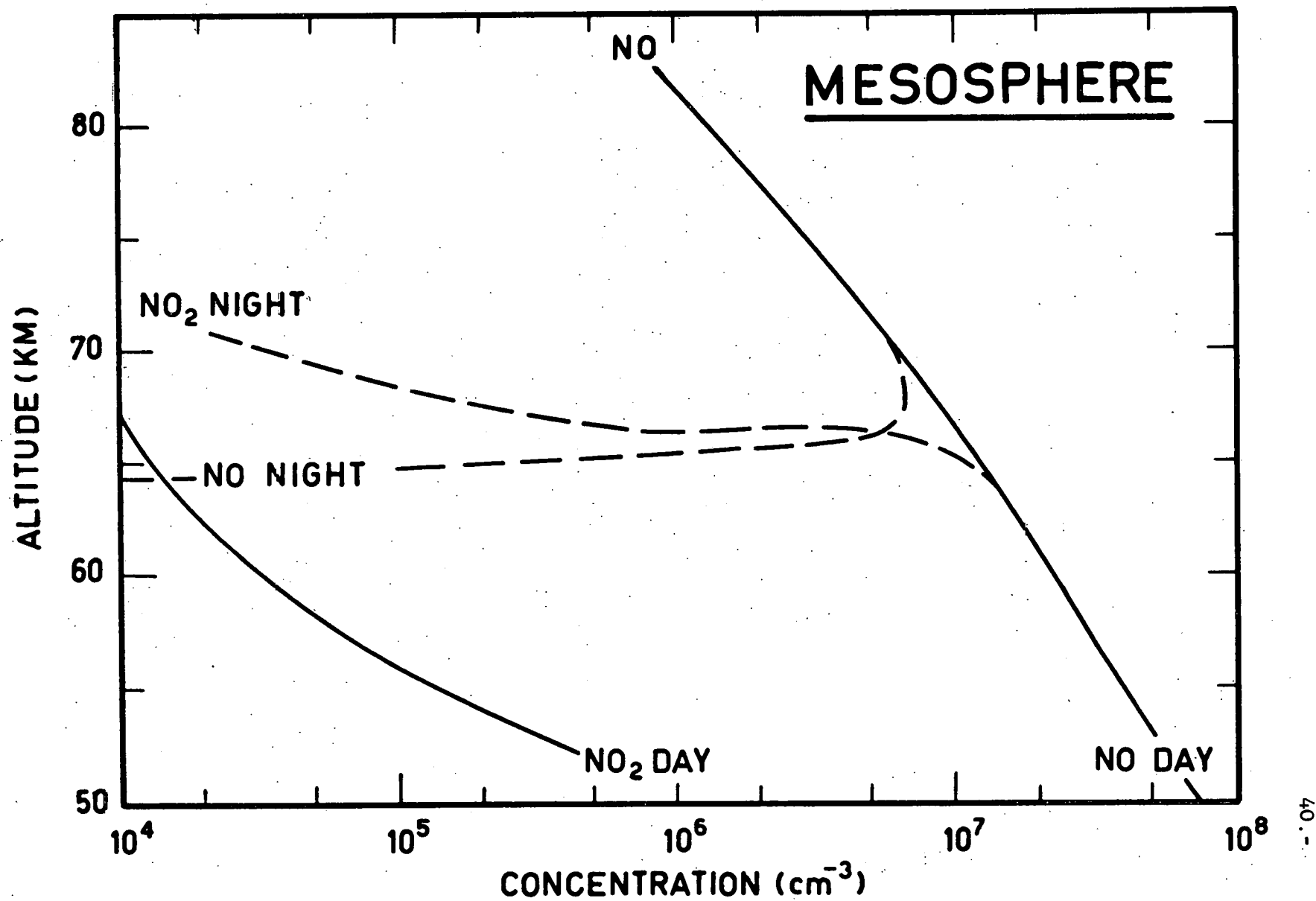
The rapid reaction [16, 57, 58, 59, 60]

FIGURE 6.

FIGURE 7.

$$H + NO_2 \rightarrow OH + NO + 30 \text{ kcal} \tag{130}$$

has a high rate coefficient with a very small, if any, activation energy b_{10}
between $1 \times 10^{-11} T^{1/2} e^{-1000/T}$ and $3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{sec}^{-1}$.

In the mesosphere, reaction (130) must be compared with reaction
(91) between atomic oxygen and nitrogen dioxide. Thus, (130) is not important
in chemical aeronomy.

A catalytic action of nitric oxide occurs in the reaction with
hydrogen atoms. The formation of HNO by three-body associations

$$H + NO + M \rightarrow HNO + 48 \text{ kcal} \tag{131}$$

for which a rate coefficient b_{11} has been measured by Clyne and Trush [61]

$$b_{11} = 1.5 \times 10^{-32} e^{+[300 \pm 100]/T} \text{ cm}^6 \text{sec}^{-1} \tag{132}$$

is followed by the bimolecular process

$$H + HNO \rightarrow NO + H_2 + 54 \text{ kcal}. \tag{133}$$

If (133) has a rate coefficient greater than $5 \times 10^{-14} \text{ cm}^3 \text{sec}^{-1}$ at
$226°K$[61] which must correspond to

$$b_{12} > 1.5 \times 10^{-11} T^{1/2} e^{-2000/T} \text{ cm}^3 \text{ sec}^{-1} \tag{134}$$

the stationary value of n(H NO) should be of the order

$$n(HNO) = 10^{-21} e^{2000/T} n(NO) \tag{135}$$

which means a negligible concentration in the mesosphere. It can be also
stated that the loss of hydrogen atoms in the mesosphere is negligible. Adopting
maximum values for the rate coefficient and using the values of n(NO) shown in
Fig. 7, it is clear that

$$- \frac{dn(H)}{dt} < 10^{-8} n(H) \tag{136}$$

Such a process affecting atomic hydrogen is not important when compared with other aeronomic reactions for hydrogen.

Reactions of nitric oxide with the perhydroxyl radicle or with hydrogen peroxide are perhaps more important in chemical aeronomy. According to Tyler[62] the bimolecular process at 630°K

$$NO + HO_2 \rightarrow OH + NO_2 + 9 \text{ kcal} \tag{137}$$

is fast relative to other reactions of HO_2. In addition, the overall reaction in which H_2O_2 is involved, written as

$$H_2O_2 + NO \rightarrow H_2O + NO_2, \tag{138}$$

shows that an aeronomic analysis is required for the transition region $H_2O_2 - HO_2 - OH$ in the lower mesosphere. Unfortunately, the additional processes which arise from the reactions between hydrogen and nitric oxide cannot be determined before the basic data on the variation of the rate coefficients are known. Calculations are too difficult and the uncertainties are still too serious to allow the correct vertical distribution to be predicted. Nevertheless, the general equilibrium will not be affected, according to (69), even if the various ratios of hydrogen oxides are different.

REFERENCES.

[1] Chapman, S., Phil. Mag., 1930, 10, 369

[2] Chapman, S., Rep. on Progress in Physics, 1943, 9, 92

[3] Nicolet, M. and Mange, P., J. Geophys. Res., 1954, 59, 15

[4] Bates, D.R. and Nicolet, M., J. Geophys. Res., 1950, 55, 301.

[5] Meinel, A.B., Astrophys. J., 1950, 111, 207 and 433.

[6] Chamberlain, J.W. and Smith C.A., J.Geophys.Res., 1959, 64, 611.

[7] Bates, D.R. and Nicolet, M., Compt. Rend. Acad. Sci., Paris, 1950, 230, 1943; Pub. Astronom. Soc. Pacific, 1950, 62, 106.

[8] Bates, D.R. and Witherspoon, A.E., Month. Notices Roy. Astronom. Soc., 1952, 112, 101

[9] Hutchinson, G.E., Chapter 8, " The Biochemistry of the Terrestrial Atmosphere", in : Kuiper, G.P. (ed.), The Solar System, vol. II, The Earth as a Planet, The University of Chicago Press, Chicago, 1954.

[10] Nicolet, M., Inst. Météor. Belgium, Mémoires, 1945, 19, 124.

[11] Bates, D.R., Ann. Geophys., 1952, 8, 194.

[12] Nicolet, M., J. Atm. Terr. Phys., 1955, 7, 152.

[13] Nicolet, M., Aeronomic chemical reactions in Physics and Medicine of the Atmosphere and Space, John Wiley and Sons, New-York, 1960.

[14] Barth, C.A., Ann. Géophys., 1964, 20,

[15] Schiff, H.I., Ann. Géophys., 1964, 20, 115.

[16] Kaufman, F., Ann. Géophys., 1964, 20, 106.

[17] Detwiler, C.R., Garret, D.L., Purcell, J.P. and Tousey, R., Ann. Géophys., 1961, 17, 9.

[18] Ditchburn, R.W. and Young, P.A., J. Atm. Terr. Phys., 1962, 24, 127.

[19] Vigroux, E., Ann. Phys., Paris, 1953, 8, 709.

[20] Inn, E.C.Y. and Tanaka, Y., J. Opt. Soc. Am., 1953, 43, 870.

[21] Hearn, A.G., Proc. Phys. Soc., 1961, 78, 932.

[22] Dütsch, H.U., in : Chemical Reactions in the Lower and Upper Atmosphere, p. 167, Interscience Publishers, New York, 1961.

[23] Paetzold,H.K., in : Chemical Reactions in the Lower and Upper Atmosphere, p. 181, Interscience Publishers, New York, 1961

[24] Eucken, A. and Patat, F., Zeit. Phys. Chem., 1936, 33B, 459.

[25] Benson, S.W. and Axworthy, A.E., Jr., J. Chem. Phys., 1957, 26, 1718.

[26] Zaslowsky, J.A., Urbach, H.B., Leighton, F., Wnuk, R.J. and Wojtowicz, J.A., J. Amer. Chem. Soc., 1960, 82, 2682.

[27] Kaufman, F., This meeting.

[28] Kockarts, G. and Nicolet, M., Ann. Géophys., 1962, 18, 269.

[29] Nicolet, M., Mém. Soc. Roy. Sci. Liège, 1962, 7, 1960.

[30] Steacie, E.W.R., in : Atomic and Free Radical Reactions, p. 601, Reinhold Publishing Corporation, New York, 1954.

[31] Wong, E.L. and Potter, A.E., Jr., J. Chem. Phys., 1963, 39, 2211.

[32] Goldberg, L. and Müller, E.A., Astrophys. J., 1953, 118, 397.

[33] Clyne, M.A.A. and Thrush, B.A., Proc. Roy. Soc., 1963, 275A, 559.

[34] Bates, D.R. and Patterson, T.N., Planet. Sp. Sci., 1961, 5, 257.

[35] Foner, S.N. and Hudson, R.L., in Advances in Chemistry Series n° 36, p. 36, American Chemical Society, Washington D.C., 1962.

[36] Knox, J.H., Ann. Rep. Progress Chem., 1962, 59, 18.

[37] Minkoff, G.J. and Tipper, C.H.F., Chemistry of Combustion Reactions, Butterworths, London, 1963.

[38] Ninth Symposium on Combustion, Academic Press, New York, 1963.

[39] Baldwin, R.R. and Mayor, L, Trans. Faraday Soc., 1960, 56, 103.

[40] Foner, S.N. and Hudson, R.L., J. Chem. Phys., 1962, 36, 2681.

[41] Mavroyannis, C. and Winkler, C.A., Canad. J. Chem., 1961, 39, 1601.

[42] Young, R.A. and Sharpless, R.L., J. Chem. Phys., 1963, 39, 1071.

[43] Callear, A.B. and Smith, I.W.M., This meeting.

[44] Clyne, M.A.A. and Thrush, B.A., Proc. Roy. Soc., 1962, 269A, 404.

[45] Basco, N. and Norrish, R.G.W., Canad. J. Phys., 1960, 38, 1769.

[46] Phillips, L.F. and Schiff, H.I., J. Chem. Phys., 1962, 37, 924.

[47] Johnston, H.S. and Crosby, H.J., J. Chem. Phys., 1954, 22, 689.

[48] Greaves, J.C. and Garvin, D., J. Chem. Phys., 1959, 30, 348.

[49] Clyne, M.A.A., Thrush, B.A. and Wayne, R.P., Trans. Faraday Soc., 1964, 60, .

[50] Ford, H.W., Canad. J. Chem., 1960, 38, 1780.

[51] Kistiakowsky, G.B. and Volpi, G.G., J. Chem. Phys., 1957, 27, 1141.

[52] Clyne, M.A.A. and Thrush, B.A., Proc.Roy. Soc., 1961, 261A, 259.

[53] Mavroyannis, C. and Winkler, C.A., in : Chemical Reactions in the Lower and Upper Atmosphere, p. 287, Interscience Publishers, New York, 1961.

[54] Chen, M.C. and Taylor, H.A., J. Chem. Phys., 1961, 34, 1344.

[55] Phillips, L.F. and Schiff, H.I., J. Chem. Phys., 1962, 36, 1509.

[56] Georgii, H.-W., J. Geophys. Res., 1963, 68, 3963.

[57] Phillips, L.F. and Schiff, H.I., J. Chem. Phys., 1962, 37, 1233.

[58] Rosser, W.A. and Wise, H.,J. Phys. Chem., 1961, 65, 532.

[59] Clyne, M.A.A. and Thrush, B.A., Trans. Faraday Soc., 1961, 57, 2176.

[60] Ashmore, P.G. and Tyler, B.J., Trans. Faraday Soc., 1962, 58, 1108.

[61] Clyne, M.A.A. and Thrush, B.A., Discussions Faraday Soc., 1962, 33, 139.

[62] Tyler, B.J., Nature, London, 1962, 195, 279.