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Aeronomic reactions of hydrogen and ozone

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FOREWORD

"Aeronomic reactions of hydrogen and ozone" was given at the 4th ESRIN - ESLAB symposium held in Frascati from July 6 to 10 1970. It will be published in the proceedings of the symposium.

AVANT-PROPOS

"Aeronomic reactions of hydrogen and ozone" est le texte d'une conférence faite au 4e symposium ESRIN - ESLAB à Frascati du 6 au 10 juillet 1970. Il sera publié dans les comptes-rendus du symposium.

VOORWOORD

"Aeronomic reactions of hydrogen and ozone" is de tekst van een voordracht gegeven tergelegenheid van het 4de symposium ESRIN - ESLAB dat plaats had in Frascati van 6 tot 10 juli 1970. Deze tekst zal gepubliceerd worden in de annalen van het symposium.

VORWORT

"Aeronomic reactions of hydrogen and ozone" ist der Text einer Konferenz die zum 4. Symposium ESRIN - ESLAB in Frascati (6. zum 10. Juli 1970) vorgestellt wurde. Der Text wird in den "Proceedings" dieses Symposium herausgegeben werden.

AERONOMIC REACTIONS OF HYDROGEN AND OZONE

by

M. NICOLET

INTRODUCTION

Forty years ago Chapman [1930] showed that the dissociation of molecular oxygen was important above 100 km and, therefore, that the aeronomic behavior of ozone was related to the dissociation of oxygen below 100 km [Chapman, 1943]. Furthermore, twenty years ago, vibrational-rotational bands of the hydroxyl radical OH, which appear in the airglow [Meinel, 1950], aroused interest in the photochemistry of hydrogen-oxygen compounds [Bates and Nicolet, 1950a ; Herzberg, 1951] and, in particular, of methane [Bates and Nicolet, 1950b] and of water vapor [Bates and Nicolet, 1950c].

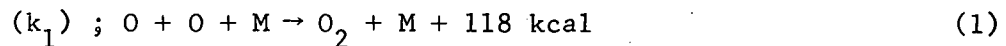
The photochemistry of atmospheric water vapor, which was studied in considerable detail by Bates and Nicolet [1950c], was difficult due to the grievous lack of reliable basic data. Our knowledge concerning the experimental rate coefficients has increased rapidly in recent years and systematic accounts can be found in several review papers published since 1963 : three-body reactions by Barth [1964] ; reactions involving nitrogen and oxygen by Schiff [1964, 1969] and reactions involving hydrogen and other minor constituents by Kaufman [1964, 1969]. A complete application to aeronomy must still await other laboratory investigations under controlled conditions which are of fundamental importance for a useful interpretation of space observations.

As far as the solar radiation and its absorption are concerned, much progress has been made since the analysis of the H₂O photodissociation in a nitrogen-oxygen atmosphere by Bates and Nicolet [1950c] who adopted a

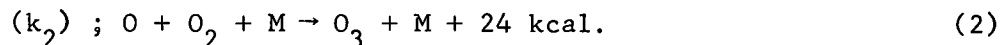
solar flux corresponding to 5000°K with the possibility of local variations of 300°K in different parts of the spectral range concerned. The influence of the N₂ absorption is negligible in the mesosphere and in the present connection, only molecular oxygen by the two systems, the Herzberg and the Schumann-Runge, plays the essential role. Recently, new results [Ackerman, Biaumé and Kockarts, this symposium] have been obtained in the region of 2100 Å to 1750 Å and these have shown that our knowledge of solar radiation and relevant absorption cross-sections must be improved.

I. OZONE FORMATION AND DISSOCIATION

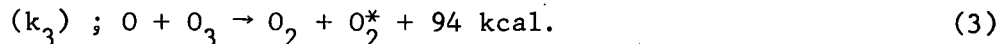
When the dissociation of molecular oxygen occurs, it is followed by the three-body recombination



or by ozone formation



Ozone is destroyed by the bimolecular process

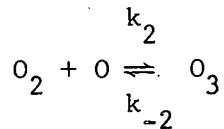


A precise knowledge of the rate coefficients k_1 , k_2 and k_3 is required in order to determine the chemical rate coefficients for the formation and destruction of atmospheric ozone. The value of k_1 seems to be known, with sufficient precision for aeronomic purposes. A recent experimental analysis [Campbell and Thrush, 1967] indicates that the molecular oxygen formation in the presence of molecular nitrogen ($M \equiv N_2$) has a rate coefficient varying with temperature. It can be expressed as

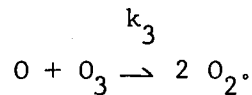
$$k_1 = 3 \times 10^{-33} (300/T)^3 n(N_2) \text{ cm}^3 \text{ sec}^{-1} \quad (4)$$

in order to represent values such as about $4 \times 10^{-33} \text{ cm}^3 \text{ sec}^{-1}$ at 273°K and $1 \times 10^{-32} \text{ cm}^3 \text{ sec}^{-1}$ at 195°K.

As far as k_2 and k_3 are concerned, the experimental values are not yet sufficiently precise for aeronomic purposes. The thermal decomposition of ozone has been studied in terms of the following mechanisms :



and



From the usual Arrhenius plot for an ozone atmosphere between 343°K and 383°K, the values of k_{-2} and $k_{-2} k_3/k_2$ have been deduced by Benson and Axworthy [1957] and lead to

$$\frac{k_2 n(M)}{k_3} = (1.4 \pm 0.14) \times 10^{-24} e^{(3300 \pm 300)/T} n(M) \quad (5)$$

in which $n(M)$ denotes the total concentration in the homosphere.

Adopting the result

$$n(M) k_2 = 3.3 \times 10^{-35} e^{950/T} n(M) \text{ cm}^3 \text{ sec}^{-1} \quad (6)$$

from measurements by Clyne, Mc Kenney and Thrush [1962], the adopted expression for k_3 is, from (5) and (6),

$$k_3 = 2.4 \times 10^{-11} e^{-2350/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (7)$$

The numerical values obtained from (5), (6) and (7) are in agreement with experimental data at 300°K [Kaufman and Kelso, 1964 and 1967 ; Mathias and Schiff, 1964 ; Hochanadel et al, 1968]. However, there is still some uncertainty in the values of the above coefficients particularly at low temperatures which correspond to those at stratospheric and mesospheric levels. Keeping the same activation energies, k_2 should be considered as a maximum and k_3 as a minimum values. There is perhaps a possibility that $\frac{1}{2} k_2$ may correspond to a minimum value and $2 k_3$ to a maximum value. An aeronomic calculation made with these two alternatives shows that the differences are not negligible. However, more important difficulties occur in the mesosphere when only a pure oxygen-nitrogen atmosphere is considered. In fact, the vertical distribution of ozone and its absolute concentration cannot be explained without the introduction of other minor constituents.

Since it is convenient to use as basic parameters the particle concentrations in the chemical problems the adoption of an atmospheric model is required. This is represented in Table I and gives the essential properties for consistent calculations, but not for a study of seasonal or latitudinal variations. The total number of molecules in a vertical column is given by the product of the concentration and the scale height, i.e

$$\int_z^{\infty} n \, dz \simeq n H \quad (8)$$

With the adopted values of the atmospheric parameters given in Table I, the rate coefficients in which ozone and oxygen are involved are given in Table II. However, before beginning a discussion of these numerical values, it is necessary to consider the photodissociation rate coefficients of O_2 and O_3 .

It can be shown that the calculated values of the O_3 concentrations are too large, particularly in the mesosphere, and that the introduction of ozone-hydrogen reactions changes the situation. However, since at least

TABLE I.- Atmospheric parameters in the stratosphere and mesosphere

Altitude (km)	Scale height (km)	Temperature (°K)	Pressure (Torr)	Total Concentration	Oxygen Concentration
15	6.20	211	8.5×10^1	3.9×10^{18}	8.1×10^{17}
20	6.45	219	3.9×10^1	1.7×10^{18}	3.6×10^{17}
25	6.70	227	1.8×10^1	7.7×10^{17}	1.6×10^{17}
30	6.95	235	8.6	3.6×10^{17}	7.4×10^{16}
35	7.45	252	4.3	1.7×10^{17}	3.5×10^{16}
40	7.95	268	2.2	8.1×10^{16}	1.7×10^{16}
45	8.15	274	1.2	4.3×10^{16}	8.9×10^{15}
50	8.15	274	6.6×10^{-1}	2.3×10^{16}	4.8×10^{15}
55	8.15	273	3.6×10^{-1}	1.3×10^{16}	2.6×10^{15}
60	7.54	253	1.9×10^{-1}	7.2×10^{15}	1.5×10^{15}
65	6.93	232	9.4×10^{-2}	3.9×10^{15}	8.2×10^{14}
70	6.32	211	4.4×10^{-2}	2.0×10^{15}	4.2×10^{14}
75	5.82	194	1.9×10^{-2}	9.6×10^{14}	2.0×10^{14}
80	5.32	177	7.9×10^{-3}	4.2×10^{14}	9.0×10^{13}
85	4.82	160	2.9×10^{-3}	1.9×10^{14}	3.7×10^{13}

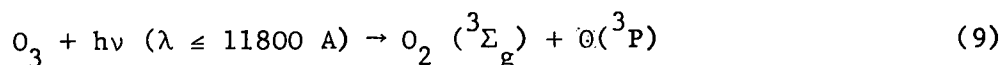
TABLE II.- Stratospheric and mesospheric rate coefficients for ozone
and oxygen reactions

Altitude (km)	$k_1 n(M)$ ($\text{cm}^3 \text{sec}^{-1}$)	$k_2 n(M)$ ($\text{cm}^3 \text{sec}^{-1}$)	k_3 ($\text{cm}^3 \text{sec}^{-1}$)	$k_2 n(M) n(O_2)$ (sec^{-1})	$k_2 n(M) n(O_2)/k_3$ (cm^{-3})
15	1.1×10^{-14}	1.2×10^{-14}	3.5×10^{-16}	9.5×10^3	2.7×10^{19}
20	5.5×10^{-15}	5.2×10^{-15}	5.2×10^{-16}	1.6×10^3	2.9×10^{18}
25	2.1×10^{-15}	1.7×10^{-15}	7.7×10^{-16}	2.7×10^2	3.5×10^{17}
30	9.8×10^{-16}	6.7×10^{-15}	1.1×10^{-15}	5.0×10^1	4.5×10^{16}
35	4.6×10^{-16}	2.4×10^{-16}	2.1×10^{-15}	8.3×10^0	3.9×10^{15}
40	2.2×10^{-16}	9.3×10^{-17}	3.8×10^{-15}	1.6×10^0	4.2×10^{14}
45	1.2×10^{-16}	4.5×10^{-17}	4.6×10^{-15}	4.0×10^{-1}	8.7×10^{13}
50	6.4×10^{-17}	2.4×10^{-17}	4.5×10^{-15}	1.2×10^{-1}	2.6×10^{13}
55	3.5×10^{-17}	1.3×10^{-17}	4.5×10^{-15}	3.5×10^{-2}	7.8×10^{12}
60	2.0×10^{-17}	1.0×10^{-17}	2.2×10^{-15}	1.5×10^{-2}	6.9×10^{12}
65	1.1×10^{-17}	7.8×10^{-18}	9.6×10^{-16}	7.6×10^{-3}	6.7×10^{12}
70	5.6×10^{-18}	6.0×10^{-18}	3.5×10^{-16}	2.5×10^{-3}	7.2×10^{12}
75	2.7×10^{-18}	4.2×10^{-18}	1.3×10^{-16}	8.5×10^{-4}	6.4×10^{12}
80	1.2×10^{-18}	3.0×10^{-18}	4.2×10^{-17}	2.7×10^{-4}	6.5×10^{12}
85	4.9×10^{-19}	2.2×10^{-18}	1.0×10^{-17}	8.1×10^{-5}	7.9×10^{12}

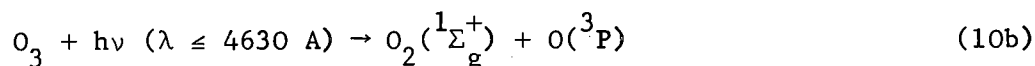
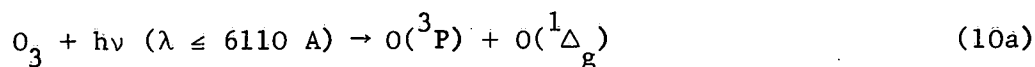
superficial agreement is obtained by taking rate coefficients which fit the observational data, it seems to us that an adopted model for the vertical distribution of ozone could more adequately describe the aeronomic processes which are involved.

In Fig. 1a and 1b the profile adopted for the distribution of the ozone concentration in the mesosphere and stratosphere corresponds to conditions which are consistent with observational data. For the height range 40-80 km, such a vertical distribution leads to a simple density distribution $e^{-0.23 z(\text{km})}$ giving $n(\text{O}_3) = 10^{12}$ at 40 km and 10^8 cm^{-3} at 80 km. From such a distribution it is possible to deduce average conditions in the stratosphere and mesosphere.

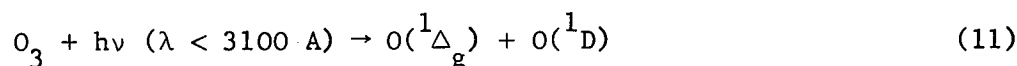
When an analysis of the ozone photodissociation is made, it is necessary to distinguish between the various products in order to know the production rate of excited atoms or molecules. For $\lambda \leq 11800 \text{ \AA}$



with O_2 and O in their normal states. In the spectral range of the Chappuis band (with predissociation) it is logical to consider that (9) represents the normal process even if the following processes, with spin changes are energetically possible



However, (10a) seems to be an important process in the Huggins band [Jones and Wayne, 1969] while



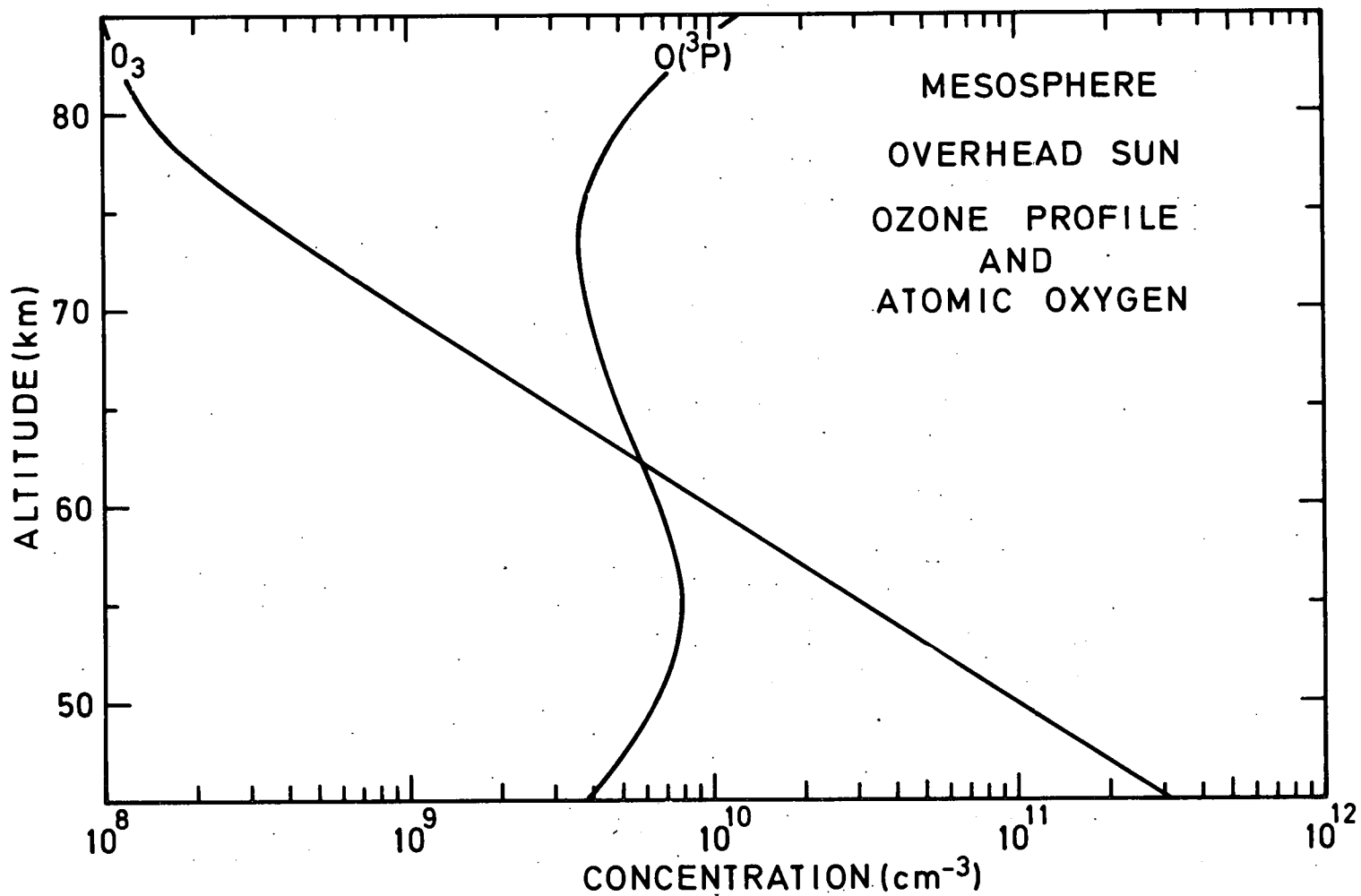


Fig. 1a.- Atomic oxygen concentration for daytime conditions in the mesosphere when the vertical distribution of the ozone concentration corresponds to 10^{11} cm^{-3} , 10^{10} cm^{-3} and 10^9 cm^{-3} at 50 km, 60 km and 70 km, respectively.

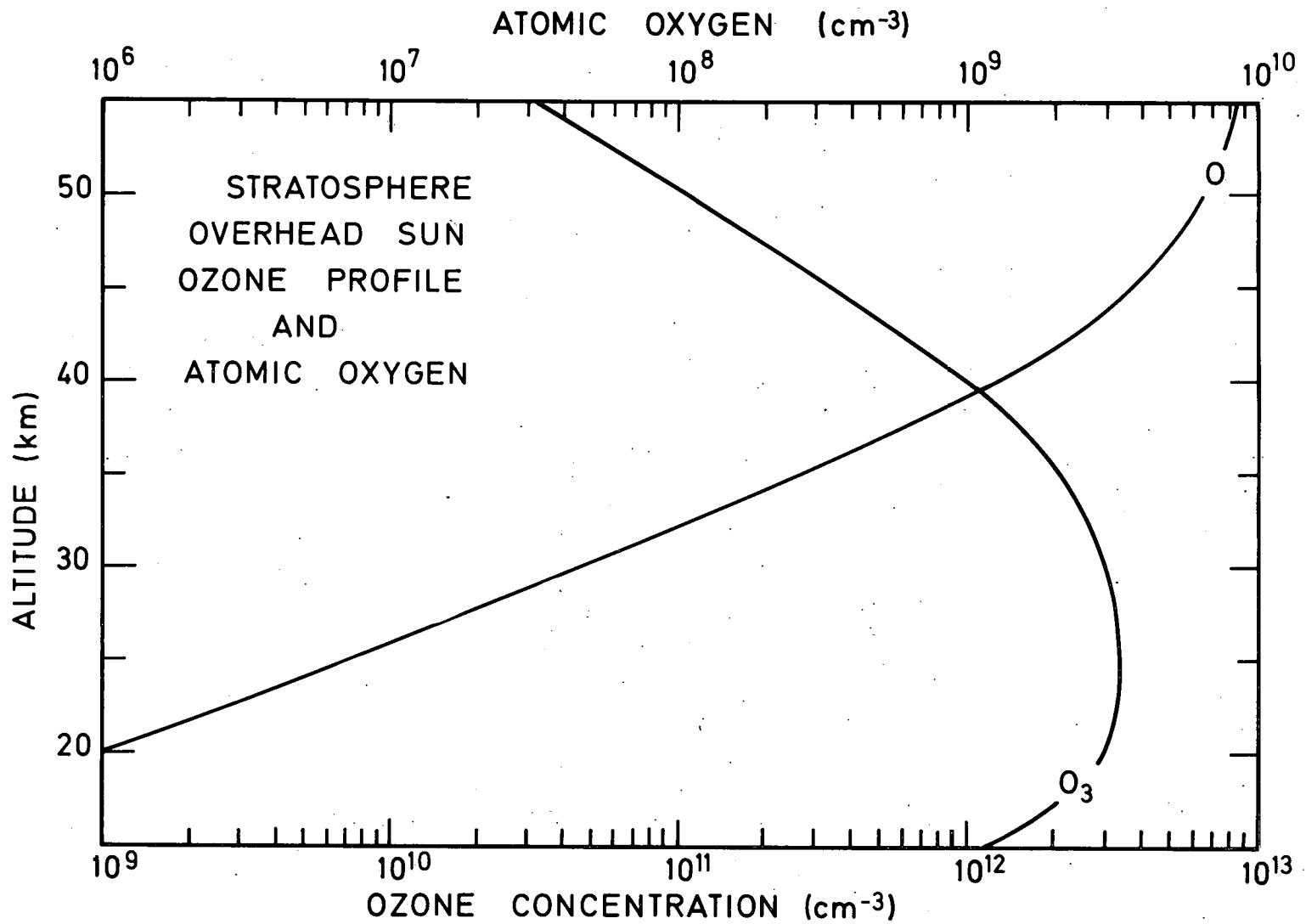
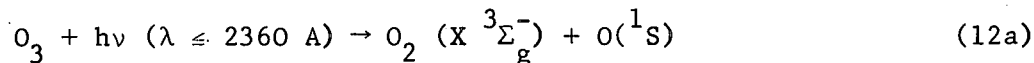


Fig. 1b.- Atomic oxygen concentration in the stratosphere for overhead sun conditions when the ozone concentration is given.

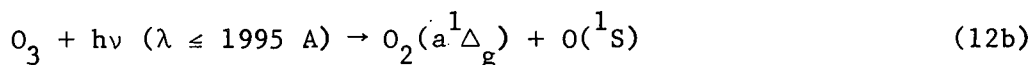
leads to a complete production of $O(^1D)$ atoms for $\lambda < 3000 \text{ \AA}$ [De More and Raper, 1966] and to 0.4 ± 0.15 of the total production at $\lambda = 3130 \text{ \AA}$.

Other processes leading to $O_2(^1\Sigma_g^+)$ and to $O(^1S)$ at shorter wavelengths should also be considered and require an experimental analysis in order to determine the exact fraction of their production by absorption in the Hartley band.

For example, the spin forbidden photodissociation at $\lambda < 2360 \text{ \AA}$



cannot have an important role since it corresponds only to a small fraction of the total photodissociation. But the spin allowed transition



may be considered at wavelengths less than 2000 \AA . However, it can be shown that the production of $O(^1S)$ atoms by (12) is small compared with that of $O(^1D)$ atoms since the solar flux is greater at 3000 \AA than at 2000 \AA .

The small absorption cross-section of the Chappuis band [Vigroux, 1953 ; Tanaka et al, 1953 ; Inn and Tanaka, 1953] which reaches only $5 \times 10^{-21} \text{ cm}^2$ at the absorption peak near 6000 \AA , leads to a photodissociation coefficient

$$J_{O_3}(\text{Chappuis}) = 3 \times 10^{-4} \text{ sec}^{-1} \quad (13)$$

for zero optical depth.

The absorption cross-section in the Huggins bands increases from about 10^{-22} cm^2 between 3500 \AA and 3600 \AA up to 10^{-19} cm^2 at 3100 \AA . This

spectral region leads to a photodissociation coefficient

$$J_{O_3} \text{ (Huggins)} = 1 \times 10^{-4} \text{ sec}^{-1} \quad (14)$$

for zero optical depth. However, since the absorption cross-section increases rapidly with decreasing wavelength, the photodissociation coefficient for the spectral range λ 3100 - 3000 A is

$$J_{O_3} \text{ (3100 - 3000 A)} \approx 2 \times 10^{-4} \text{ sec}^{-1} \quad (15)$$

for zero optical depth.

The total photodissociation coefficient for zero optical depth is

$$J_{O_3} = 10^{-2} \text{ sec}^{-1} \quad (16)$$

corresponding practically to the absorption of solar radiation of $\lambda > 2300$ A for which the absorption cross-section in the Hartley band is greater than $5 \times 10^{-18} \text{ cm}^2$. Since the continuous absorption of molecular oxygen begins at $\lambda < 2420$ A, it can be said that at least 90 % of the photodissociation coefficient of ozone depends on its own absorption, i.e.

$$J(O_3) \approx J_{\infty}(O_3) e^{-\tau(O_3)} \quad (17)$$

where $J_{\infty}(O_3)$ is the photodissociation coefficient for zero optical depth and $\tau(O_3)$ the optical depth.

With the adopted distribution of the ozone concentration (Fig.1) the various dissociation coefficients are easily determined. Fig. 2 shows the photodissociation coefficients in the stratosphere where the optical depth becomes important. The total dissociation coefficient $J(O_3)$ decreases

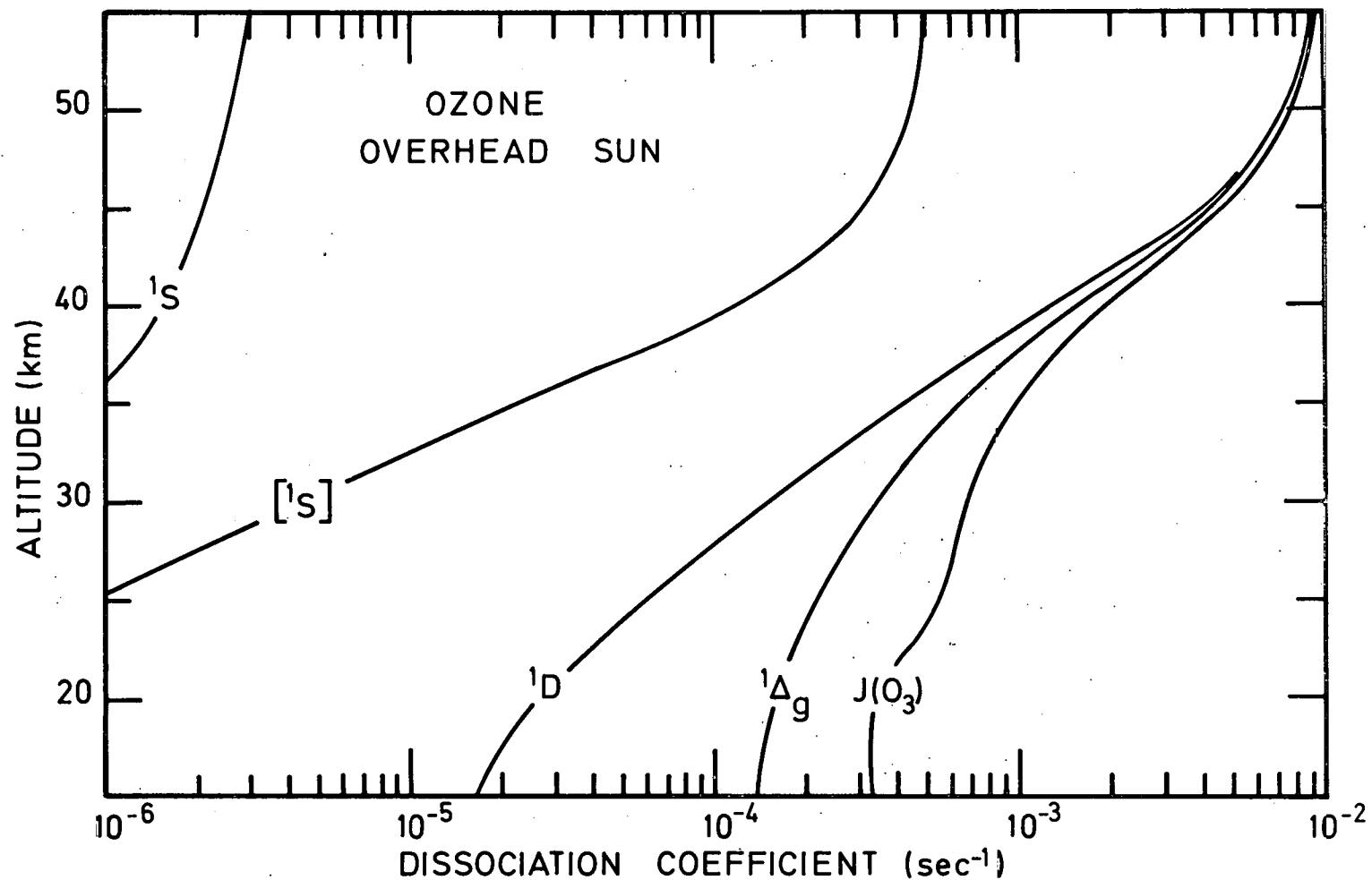


Fig. 2.- Photodissociation coefficients of stratospheric ozone for overhead sun conditions. Curve $J(O_3)$ is the total photodissociation involving all processes. Curve ${}^1\Delta_g$ is the production coefficient of oxygen molecules in the first excited electronic level ${}^1\Delta_g$. Curve 1D is the production coefficient of oxygen atoms in the metastable state 1D . Curve $[{}^1S]$ would correspond to a maximum production of $O({}^1S)$ atoms if there were no restriction with such a spin forbidden process. Curve 1S corresponds to the simultaneous maximum production of $O({}^1S)$ and $O_2({}^1\Delta)$.

from about 10^{-2} sec^{-1} in the mesosphere to about $3 \times 10^{-4} \text{ sec}^{-1}$ in the lower stratosphere where the photodissociation is due to the Chappuis band. The direct production of excited oxygen molecules in the ${}^1\Delta_g$ state is almost equivalent to the total photodissociation except in the lower stratosphere. As far as the production of excited oxygen in the 1D and 1S states is concerned, only the $O({}^1D)$ production is sufficiently important to be considered. However, the photodissociation coefficient decreases rapidly in the lower stratosphere due to the important absorption in the Hartley band.

The production of such excited atoms and molecules varies with the solar zenith angle which leads to a rapid decrease from the stratopause to the tropopause. The production of $O({}^1D)$ atoms and $O_2({}^1\Delta_g)$ molecules by the ozone photodissociation for various solar zenith angles is illustrated in Fig. 3 and Fig. 4. Molecular oxygen in the first excited state is produced during the day with a rate between 10^8 and 10^9 molecules $\text{cm}^{-3} \text{ sec}^{-1}$ in the whole of the stratosphere. With a quenching coefficient

$$k_Q({}^1\Delta_g) = 4.4 \times 10^{-19} \text{ cm}^3 \text{ sec}^{-1}$$

corresponding to the quenching by molecular oxygen [Clark and Wayne, 1969], the photoequilibrium concentration is very high. With the ozone profile given in Fig. 1 and the production rates illustrated in Fig. 4, the photoequilibrium concentrations are shown in Fig. 5. For daytime conditions the concentration peak in the neighborhood of the stratopause has a value between 3×10^{10} and 7×10^{10} $O_2({}^1\Delta_g)$ molecules cm^{-3} . At the horizon a concentration of the order of 10^{10} cm^{-3} near 60 km corresponds to a maximum for photoequilibrium conditions. Such theoretical values which correspond to observational data [Evans and Llewellyn, 1970] show that the photolysis of ozone in the Hartley band (reaction 11) is the primary process as originally proposed by Vallance Jones and Gattinger [1963]. Above the mesopause there is an increase of the $O_2({}^1\Delta_g)$ concentration which is due to an increase, in the lower thermosphere, of the ozone concentration in photoequilibrium with atomic oxygen in a sunlit

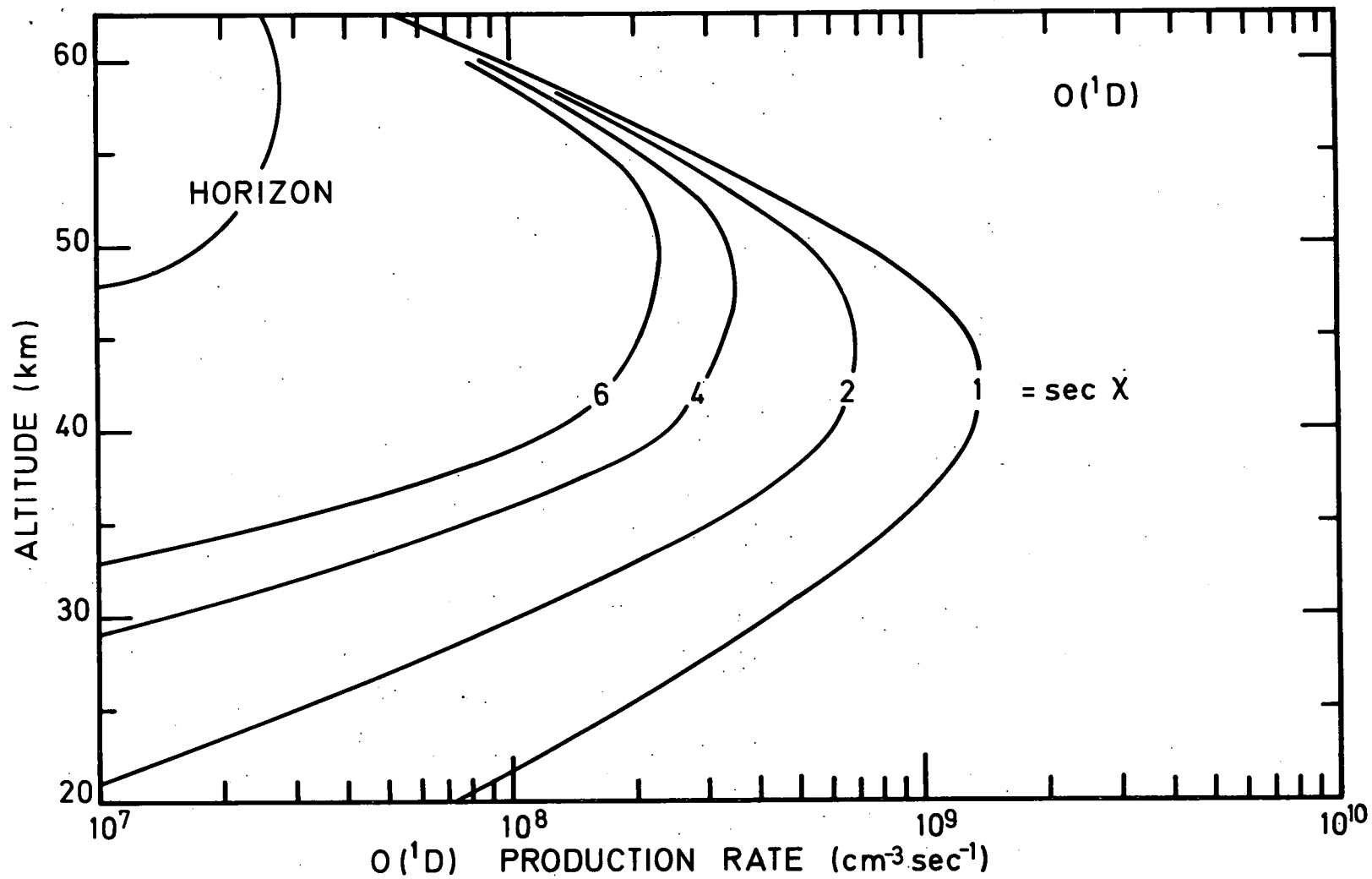


Fig. 3.- Production rate of oxygen atoms in their first excited state ¹D for various solar zenith angles. From sec χ = 1, overhead sun conditions, to horizon, χ = 90°.

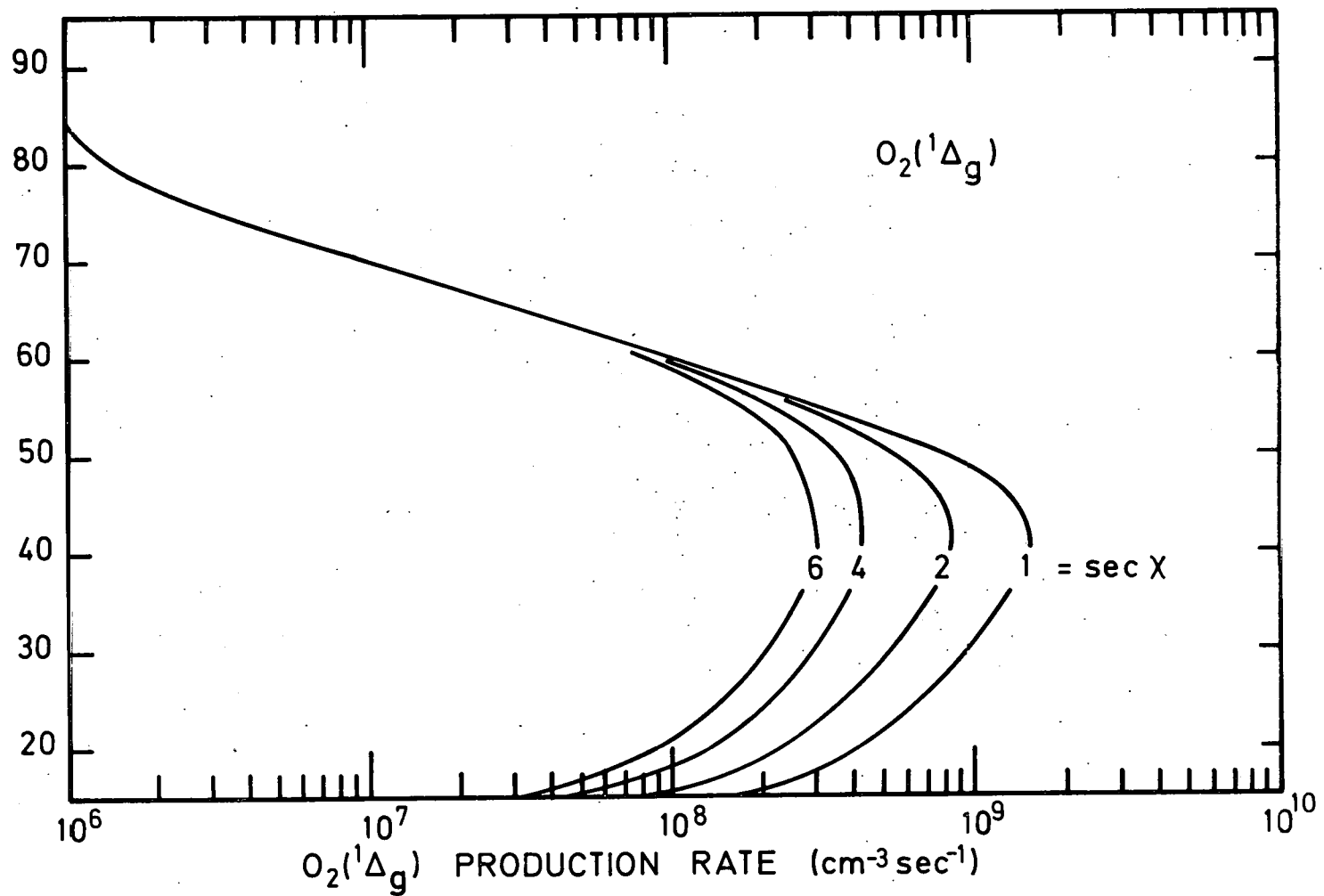


Fig. 4.- Production rate of molecular oxygen in the first excited electronic level $^1\Delta_g$ for various solar zenith angles.

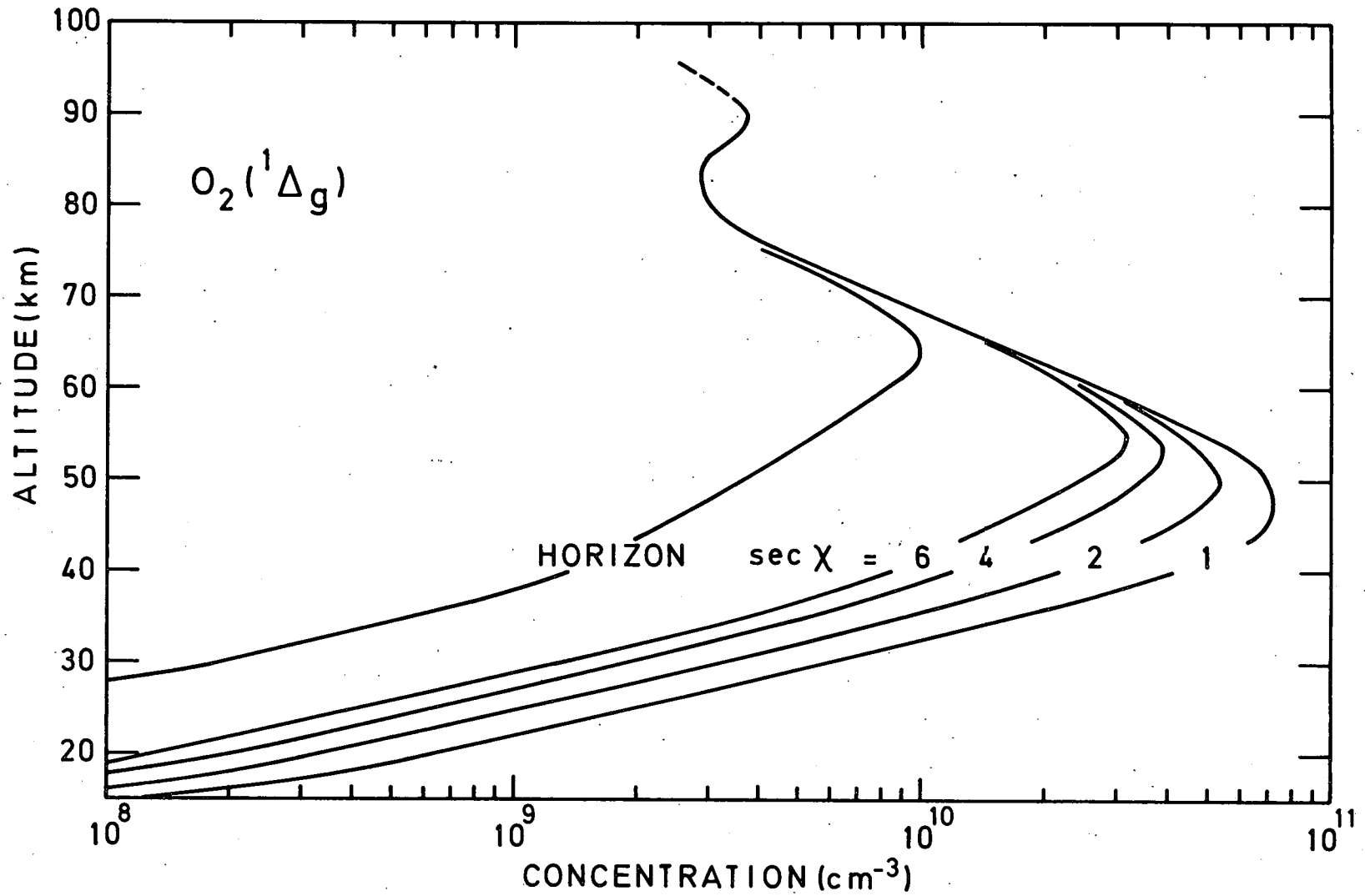


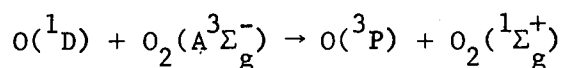
Fig. 5.- Concentration of $O_2(^1\Delta_g)$ molecules corresponding to photoequilibrium conditions for various solar zenith angles.

atmosphere, and in chemical equilibrium with atomic hydrogen in nighttime conditions.

The production of the $O(^1D)$ atoms by the photolysis process of the stratospheric and mesospheric ozone is also important (Fig. 3). However, the variation with the solar zenith angle is more important for the production of $O(^1D)$ atoms than for that of $O_2(^1\Delta_g)$ molecules. Furthermore, the quenching rate is also more important. Several experimental determinations have been published [DeMore and Raper, 1964 ; Snelling and Bair, 1967 ; Young and Black, 1967 ; Young et al, 1968 ; Noxon, 1970 ; Biedenkapp and Bair, 1970 ; DeMore, 1970]. The following working value for the whole homosphere is adopted here

$$k_Q(^1D) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}.$$

This is an average value between the maximum value $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ and the minimum value $2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. It must be pointed out that molecular oxygen is excited to its $b^1\Sigma_g^+$ state in a reaction with $O(^1D)$ atoms



with a near unitary efficiency [Young and Black, 1967 ; Noxon, 1970 ; Clark, 1970].

With the average value $k_Q(^1D) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, the production rate of $O(^1D)$ atoms illustrated in Fig. 3 leads to the photoequilibrium concentrations for various solar zenith angles shown in Fig. 6. The peak concentration of more than 10^2 cm^{-3} occurs near the stratopause for solar zenith angles where $\sec \chi \leq 6$. At the mesopause, the concentration of $O(^1D)$ begins to increase again in consequence of the photodissociation of O_2 in the Schumann-Runge continuum.

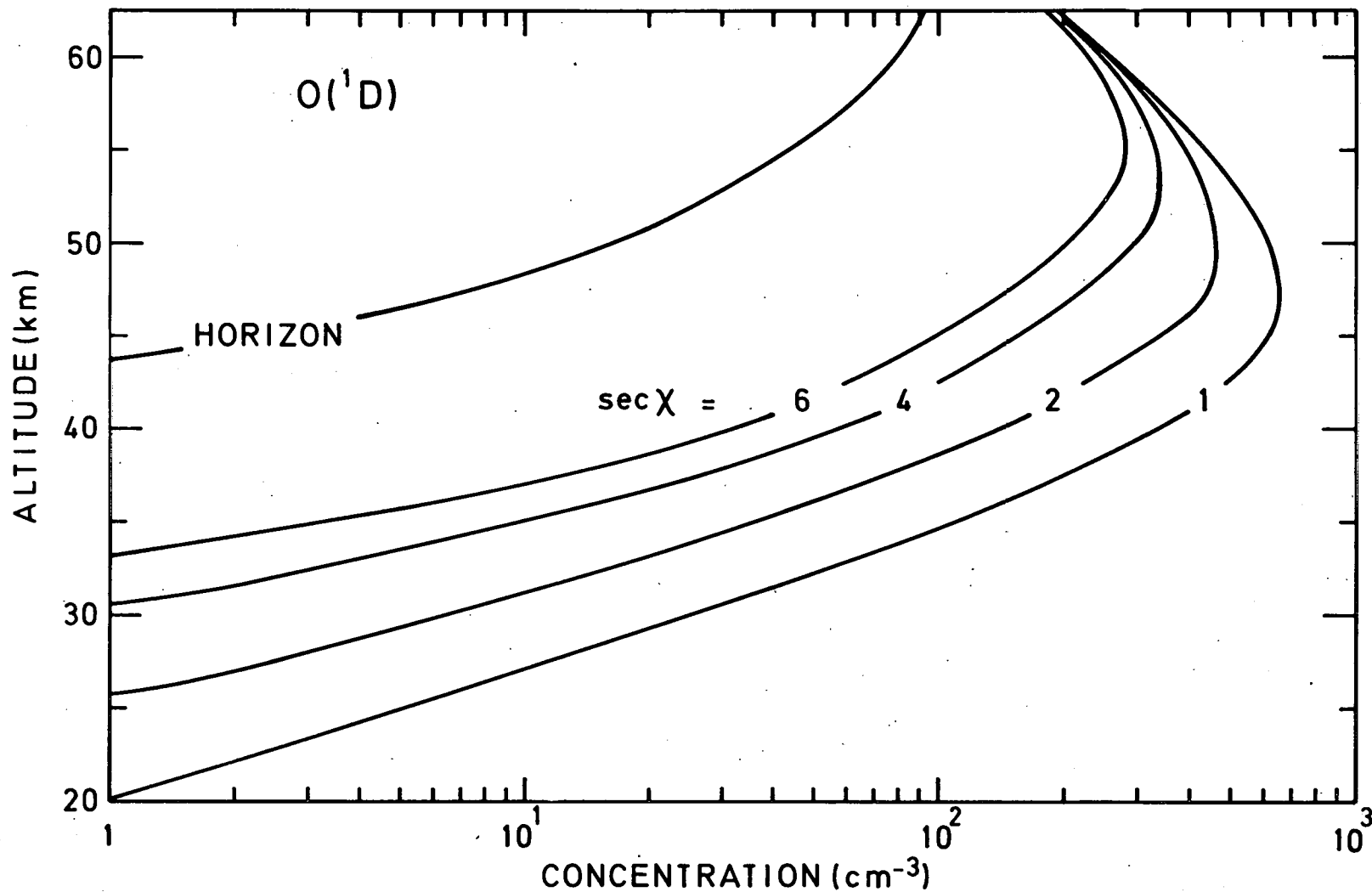


Fig. 6.- Concentrations of $O(^1D)$ atoms for various solar zenith angles.

As far as the $O(^1S)$ atoms are concerned, their low collisional deactivation with N_2 [Filseth et al, 1970]

$$k_Q(^1S, N_2) < 2 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$$

and their moderate deactivation by O_2 [Filseth et al, 1970 ; Black et al, 1969] are not sufficient to lead to important $O(^1S)$ concentrations since the production rate is too low. In any case, an oxidizing reaction with $O(^1S)$ atoms would require a rate coefficient much too great as compared with the normal rate coefficient with $O(^1D)$.

II. THE OXYGEN DISSOCIATION

As far as molecular oxygen is concerned, its photodissociation must be considered for aeronomic purposes as follows :



with two oxygen atoms in the normal state. The absorption cross-section in the Herzberg continuum is very small near the threshold, being only of the order of 10^{-24} cm^2 and becoming 10^{-23} cm^2 near 2050 A [A. Vassy, 1941 ; Ditchburn and Young, 1962 ; Shardanand, 1970]. The contribution from the Herzberg continuum to the photodissociation rate is essentially constant in the mesosphere since there is practically no absorption ; it is

$$J_{O_2}(\text{Herzberg}) = 1.3 \times 10^{-9} \text{ sec}^{-1} \quad (19a)$$

In the spectral range of the Schumann-Runge bands ($v' > 3$), where predissociation occurs, the absorption is extremely variable. The relevant cross-sections have been determined by Ackerman, Biaumé and Kockarts (1970). In using the results, allowance must, of course, be made for the effect of

temperature (cf Kockarts, this symposium, for the optical depth in the stratosphere and mesosphere and Ackerman for solar radiation data). At the mesopause, the photodissociation coefficient for the spectral range of the Schumann-Runge bands is

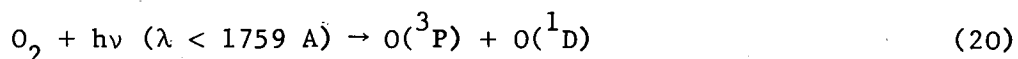
$$J_{O_2}(\text{Schumann-Runge bands})_{85 \text{ km}} = 1.7 \times 10^{-8} \text{ sec}^{-1}, \quad (19b)$$

and at the stratopause,

$$J_{O_2}(\text{Schumann-Runge bands})_{50 \text{ km}} = 1.7 \times 10^{-10} \text{ sec}^{-1} \quad (19c)$$

for an overhead sun.

The continuum to which the Schumann-Runge system converges



leads to an excited atom 1D . For zero optical depth the photodissociation coefficients are

$$J_{O_2}(\text{Schumann-Runge continuum}) = 3.7 \times 10^{-6} \text{ sec}^{-1}, \quad (21a)$$

and at 100 km

$$J_{O_2}(\text{Schumann-Runge continuum})_{100 \text{ km}} = 3.7 \times 10^{-7} \text{ sec}^{-1}. \quad (21b)$$

With such small values for the photodissociation coefficient it is certain that molecular oxygen cannot be in photochemical equilibrium in the thermosphere [Nicolet and Mange, 1954 ; Nicolet, 1954].

Finally, the absorption of Lyman- α at 1215.7 \AA by molecular oxygen must be considered since its energy is of the order of several $\text{ergs cm}^{-2} \text{ sec}^{-1}$.

With a flux of 3×10^{11} photons $\text{cm}^{-2} \text{sec}^{-1}$ and an absorption cross-section of 10^{-20}cm^2 [Watanabe, 1958], the rate is

$$J_{\text{O}_2}(\text{Lyman-}\alpha) = 3 \times 10^{-9} \text{sec}^{-1}. \quad (22)$$

In the thermosphere (see Fig. 7a), the principal process in the O_2 photodissociation is due to the absorption in the Schumann-Runge continuum; the effects of Lyman- α and of the Herzberg continuum are negligible. The predissociation process in the Schumann-Runge bands begins to play a role near the mesopause and becomes very important in the mesosphere. The Fig. 7b shows the transition from a dissociation at the mesopause through the predissociation of the bands of the Schumann-Runge system to a photodissociation by absorption in the Herzberg continuum at the stratopause. For this reason, the calculation of the photodissociation of molecular oxygen in the mesosphere requires the precise absorption cross-sections determined by Ackerman, Biaumé and Kockarts [1970]. It is not possible to use a constant absorption cross-section of the Schumann-Runge bands in order to determine the exact effect of the dissociation of molecular oxygen and other constituents such as H_2O . However, in the specific case of O_2 a constant cross-section corresponding to an optical depth of about 1 can fit the dissociation rate in the mesosphere while average cross-sections corresponding to $\tau > 1$ lead to too small photodissociation coefficients.

The photodissociation of molecular oxygen reaches a peak near the stratopause (Fig. 8) with a production rate of about $10^7 \text{cm}^{-3} \text{sec}^{-1}$ at 40 km for an overhead sun, and of about $10^6 \text{cm}^{-3} \text{sec}^{-1}$ at 60 km when the sun is at a solar zenith angle of about 90° . Fig. 8 shows the importance of variation of the O_2 dissociation in the stratosphere with the variation of the solar zenith angle.

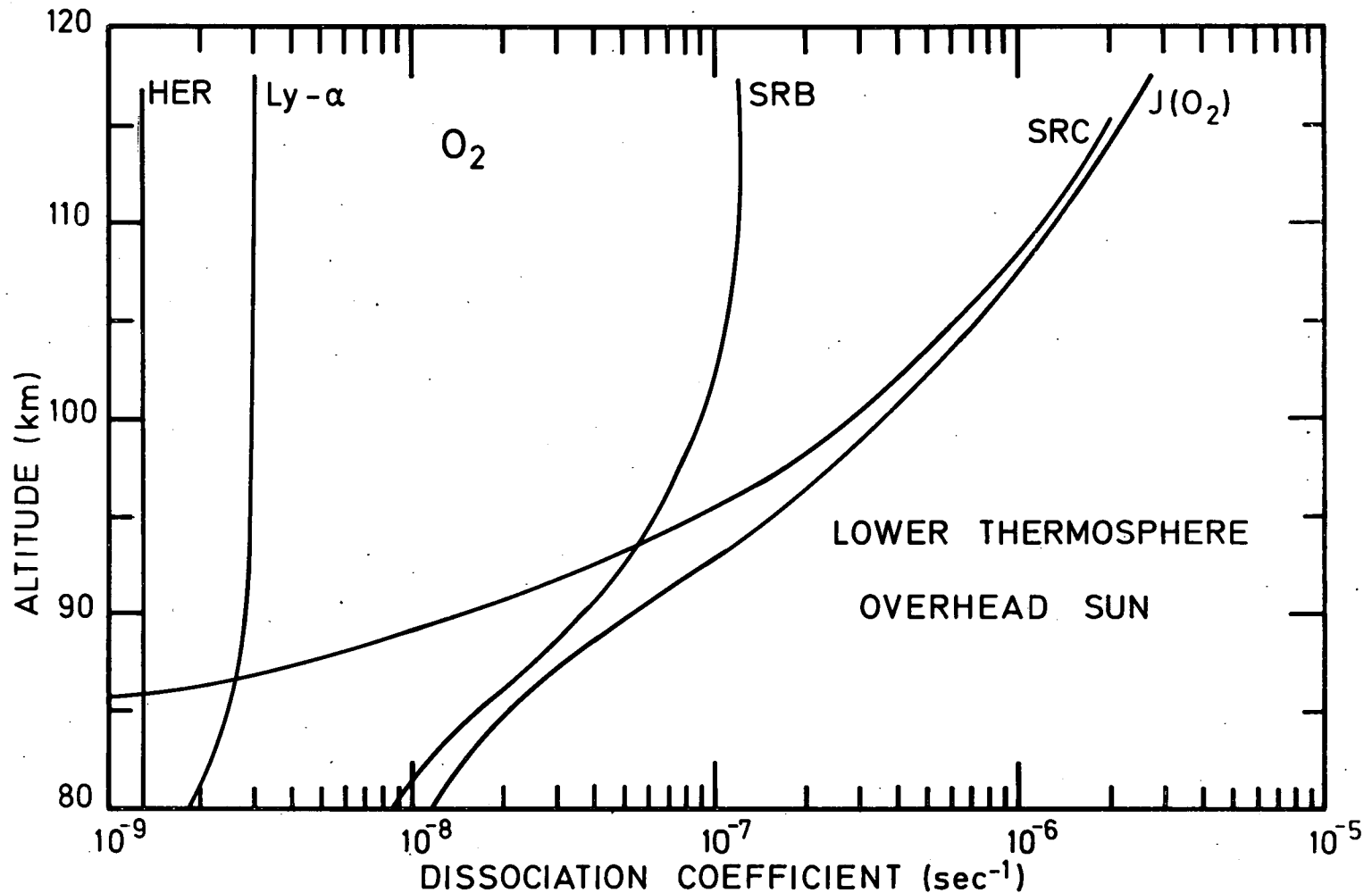


Fig. 7a.- Photodissociation coefficient of oxygen molecule in the lower thermosphere. The total photodissociation [curve $J(O_2)$] in the whole of the thermosphere depends on the absorption in the Schumann-Runge continuum (curve SRC). Near the mesopause, the spectral region of the Schumann-Runge bands (curve SRB) begins to play the principal role. The Herzberg continuum (curve HER), and Lyman- α (curve Ly α) do not play any practical role.

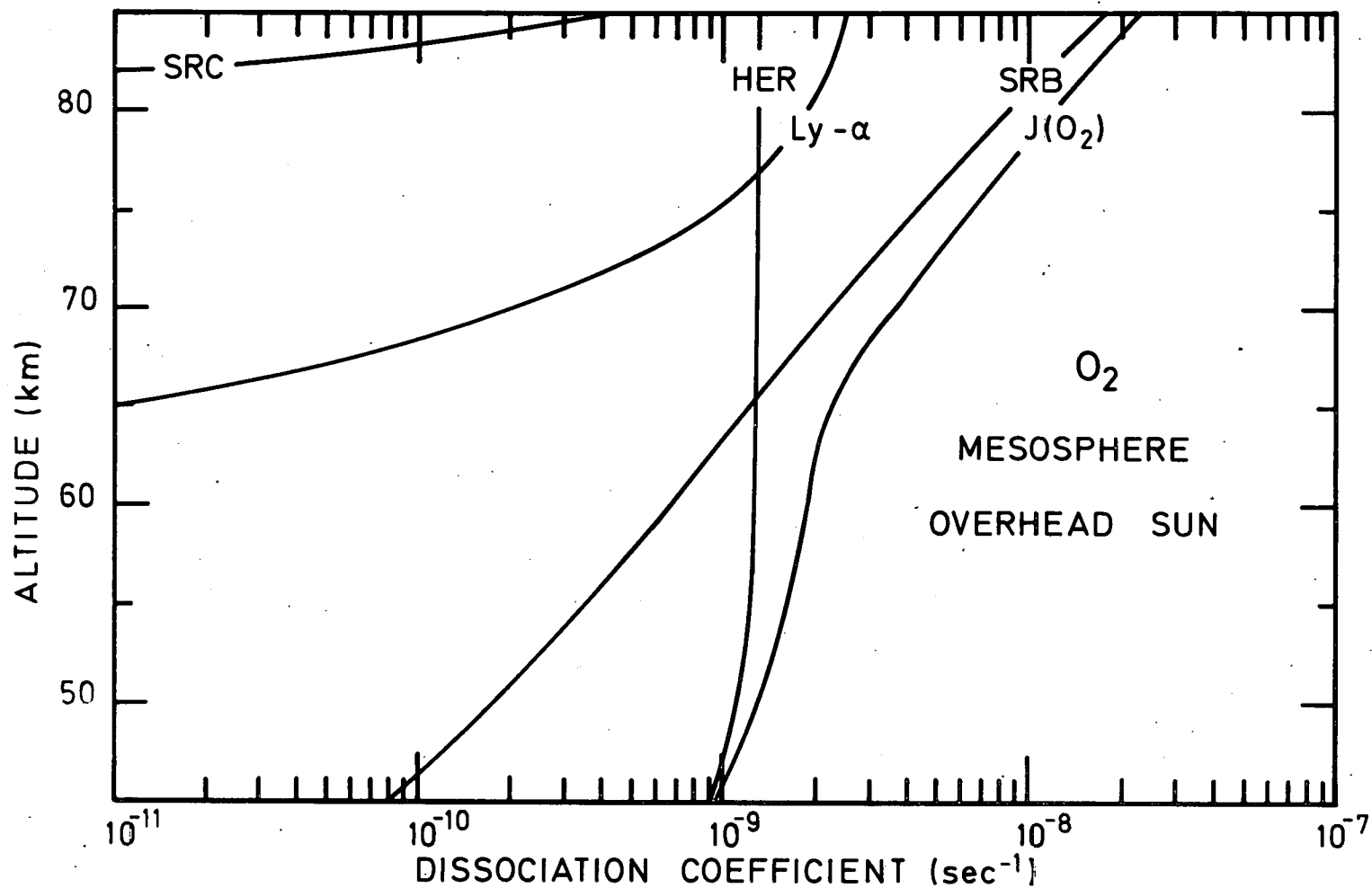


Fig. 7b.- Photodissociation coefficient of molecular oxygen in the mesosphere for overhead sun conditions. In the upper part of the mesosphere the major role is played by the region of the Schumann-Runge bands (curve SRB). Above the stratopause the Herzberg continuum is involved (curve HER).

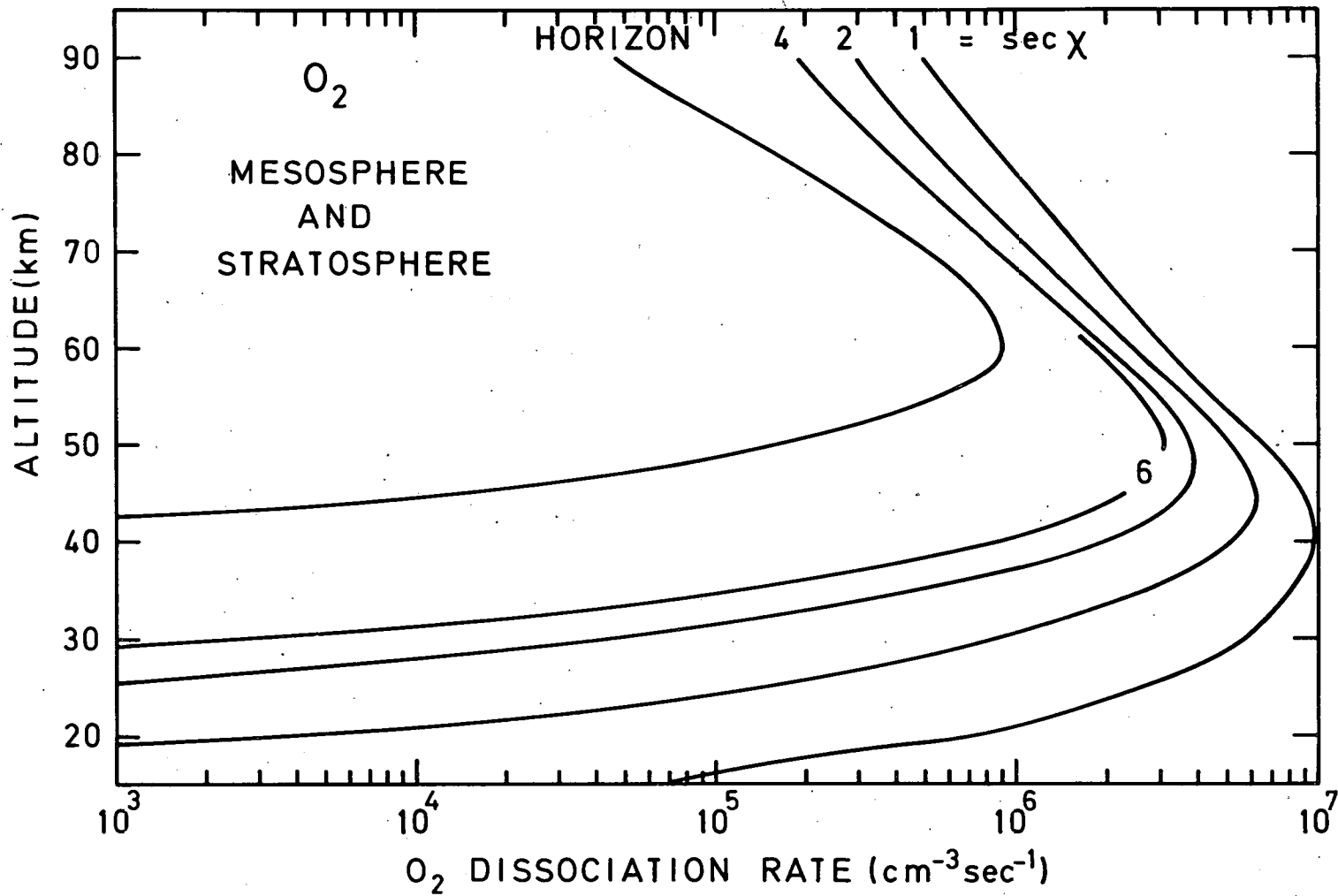


Fig. 8.- Photodissociation rate of molecular oxygen for various solar zenith angles. From overhead sun conditions, $\sec \chi = 1$, to $\chi = 90^\circ$, horizon.

III. CONDITIONS IN A PURE OXYGEN ATMOSPHERE

Considering now the theoretical problem of oxygen dissociative and ozone formation, the equations governing the rates of change of the concentrations $n(O)$ and $n(O_3)$ are

$$\begin{aligned} \frac{dn(O)}{dt} + 2k_1 n(M) n^2(O) + k_2 n(M) n(O_2) n(O) + k_3 n(O_3) n(O) \\ = 2 n(O_2) J_2 + n(O_3) J_3 \end{aligned} \quad (23)$$

$$\frac{dn(O_3)}{dt} + n(O_3) J_3 + k_3 n(O) n(O_3) - k_2 n(M) n(O_2) n(O) = 0 \quad (24)$$

which lead to the general form

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1 n(M) n^2(O) + 2k_3 n(O_3) n(O) = 2n(O_2) J_2, \quad (25)$$

where J_2 and J_3 are the photodissociation coefficients of O_2 and O_3 , respectively.

In the thermosphere and mesosphere where the photodissociation coefficient of O_3 is high : $10^{-3} \leq J \leq 10^{-2} \text{ sec}^{-1}$, there is a daytime photoequilibrium for ozone. Thus, from (24),

$$n(O_3) [J_3 + k_3 n(O)] = k_2 n(M) n(O_2) n(O) \quad (26a)$$

With $k_3 \leq 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ (cf Table II), the following approximation can be made

$$\frac{n(O_3)}{n(O)} = \frac{k_2 n(M) n(O_2)}{J_3} \quad (26b)$$

since $n(O) \leq 10^{12} \text{ cm}^{-3}$. At the mesopause level, equation (25) becomes, using (26b),

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

The time τ_0 which is required in a sunlit atmosphere to reach about 50 % of the photochemical equilibrium value (or to reach 80 % from 50 %) is given by

$$\tau_0(50\%) = 0.275 \left\{ \left[k_1 n(M) + \frac{k_3 k_2 n(M) n(O_2)}{J_3} \right] n(O_2) J_2 \right\}^{1/2} \quad (28)$$

or

$$\tau_0(50\%) = 0.275 n_*(O)/n(O_2) J_2 \quad (29)$$

if $n_*(O)$ is the photochemical equilibrium concentrations.

Application of (29) leads to the following times

Altitude (km)	90	85	80	75	70
Time (hours)	200	90	32	12	4

Thus, at the mesopause and above, in the lower thermosphere, the vertical distribution of the atomic oxygen concentration will depend on the relative importance of atmospheric transport conditions as compared with chemical equilibrium conditions. The introduction of ozone-hydrogen reactions can change the situation [Bates and Nicolet, 1950c, 1965 ; Nicolet 1964, 1966]

and various studies [Hampson, 1966 ; Hunt, 1966 ; Hesstvedt, 1968 ; Crutzen, 1969] show how the ozone behavior in the mesosphere is affected by hydrogen compounds.

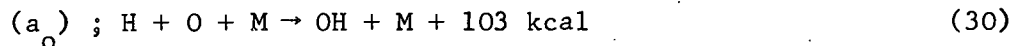
With the numerical values used in Tables I and II and the results given in various figures, it is possible to adopt the various parameters for an idealized atmosphere. Since such an atmosphere exhibits the general aeronomic features found in the stratosphere, mesosphere and lower thermosphere, Table III gives data which are required in the subsequent discussion of the reaction of the various hydrogen-oxygen compounds.

IV. HYDROGEN-OXYGEN ATMOSPHERE

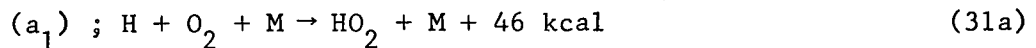
A hydrogen-oxygen atmosphere is very complicated. However, when the less probable reactions are eliminated, it is possible to have a general idea of the role of the principal reactions.

The reactions involving only a single hydrogen atom (free or combined) and one of the allotropic forms of oxygen are as follows :

The three-body reaction of atomic hydrogen with atomic oxygen



is unimportant as compared with



which has a rate coefficient [Clyne and Thrush, 1963b] taken for aeronomic purposes as

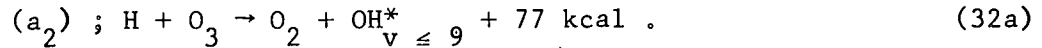
TABLE III.- Atmospheric parameters in the stratosphere and mesosphere

(overhead sun conditions)

Altitude (km)	$n(O_2)$ (cm^{-3})	$n(O_2) J_2$ ($cm^{-3} sec^{-1}$)	$n(O_3)$ (cm^{-3})	$n(O_3) J_3$ ($cm^{-3} sec^{-1}$)	$n[O(^3P)]$ (cm^{-3})	$n[O(^1D)]$ (cm^{-3})
85	3.7×10^{13}	7.3×10^5	1.0×10^8	1.0×10^6	3.0×10^{10}	1.2×10^2
80	9.0×10^{13}	1.2×10^6	1.4×10^8	1.4×10^6	1.4×10^{10}	7.0×10^1
75	2.0×10^{14}	1.5×10^6	3.2×10^8	3.2×10^6	3.8×10^9	6.7×10^1
70	4.2×10^{14}	1.7×10^6	1.0×10^9	1.0×10^7	4.0×10^9	9.6×10^1
65	8.2×10^{14}	2.2×10^6	3.2×10^9	3.2×10^7	5.0×10^9	1.5×10^2
60	1.5×10^{15}	3.0×10^6	1.0×10^{10}	9.9×10^7	6.5×10^9	2.6×10^2
55	2.6×10^{15}	4.3×10^6	3.2×10^{10}	2.9×10^8	8.4×10^9	4.4×10^2
50	4.8×10^{15}	6.6×10^6	1.0×10^{11}	7.7×10^8	6.5×10^9	6.1×10^2
45	8.9×10^{15}	9.0×10^6	3.2×10^{11}	1.5×10^9	3.7×10^9	6.0×10^2
40	1.7×10^{16}	9.7×10^6	1.0×10^{12}	1.9×10^9	1.2×10^9	3.3×10^2
35	3.5×10^{16}	8.1×10^6	2.0×10^{12}	1.9×10^9	2.4×10^8	1.0×10^2
30	7.4×10^{16}	6.7×10^6	2.9×10^{12}	2.0×10^9	3.9×10^7	2.5×10^1
25	1.6×10^{17}	2.9×10^6	3.2×10^{12}	1.8×10^9	6.7×10^6	5.0×10^0
20	3.6×10^{17}	8.0×10^5	2.9×10^{12}	1.4×10^9	9.4×10^5	9.0×10^{-1}

$$a_1 n(M) = 3.3 \times 10^{-33} e^{800/T} n(N_2, O_2) \text{ cm}^3 \text{ sec}^{-1} \quad (31b)$$

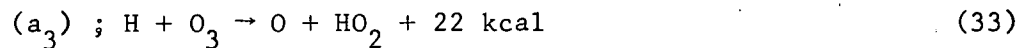
Another important loss process for atomic hydrogen is also



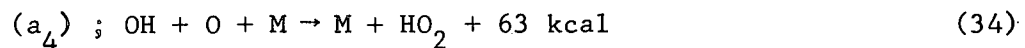
It is the Bates-Nicolet process, introduced for the interpretation of the OH airglow, which is observed in the lower thermosphere and perhaps also in the upper mesosphere. Its rate coefficient [Philips and Schiff, 1962; Kaufman 1964, 1969] with practically no activation energy is taken as

$$a_2 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (32b)$$

The production of hydroperoxyl radicals by

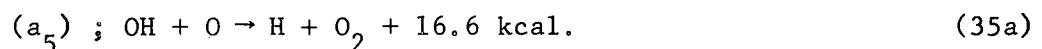


with a rate coefficient a_3 which has not been measured, and by a three-body association



with a conventional value of the three-body rate coefficient a_4 , is neglected compared with reaction (31).

An important reaction which forms a chain leading to the formation of oxygen molecules in conjunction with (32) is the bimolecular process

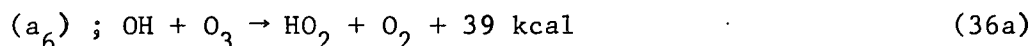


The rate coefficient [Clyne and Thrush, 1963a ; Kaufman 1964, 1969]

$$a_5 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (35b)$$

leads to the value $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K . Thus, reactions (32) and (35) show that hydrogen acts as a catalyst for the destruction of odd oxygen atoms and will affect the atomic oxygen (and ozone) distributions.

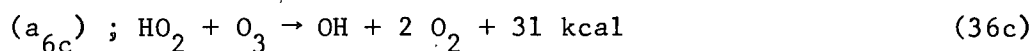
Other reactions involve hydroxyl radicals and ozone. The reaction



competes with (35) where atomic oxygen has too small a concentration (stratosphere) as compared with the ozone concentration. No direct measurement of the rate coefficient has been reported. Since an upper limit at room temperature should be of the order of $5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ [Kaufman 1964, 1969] an activation energy of only 3 kcal leads to

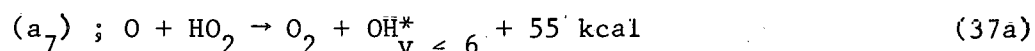
$$a_6 = 1.5 \times 10^{-12} T^{1/2} e^{-1500/T} \text{ cm}^3 \text{ sec}^{-1} \quad (36b)$$

which gives $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at the stratopause and $7.5 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ at the tropopause (190°K). An experimental analysis of this reaction is required since it has been introduced in various calculations to explain the photolysis of ozone in the presence of water vapor. Furthermore, another reaction has been introduced by various authors



in which ozone and hydroperoxyl radicals react in order to explain the OH - catalysed chain decomposition of ozone. Such a reaction requires the simultaneous breaking of the bonds OH - O and $\text{O}_2 - \text{O}$ and cannot be introduced in aeronomic calculations [Nicolet, 1970].

The principal reaction leading to OH involves atomic oxygen [Kaufman, 1964]



for which a rate coefficient

$$a_7 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (37b)$$

identical to a_5 is adopted in order to simplify the aeronomic analysis, even if it is perhaps too high by a factor of two.

In addition to these various collision processes, there is a possibility of dissociation of the hydroxyl and hydroperoxyl radicals



Such a reaction will be ignored here ($a_8 = 0$), even if there is a possibility of a dissociation due to the predissociation of the $A^2 \Sigma^+$ state for levels $v > 0$ [Smith, 1970].

Nothing is known about the photodissociation of perhydroxyl. If a comparison is made with H_2O_2 for which the photodissociation rate for zero optical depth is $J_{\text{H}_2\text{O}_2} = 1.4 \times 10^{-4} \text{ sec}^{-1}$ and with NO_2 for which $J_{\text{NO}_2} = 3.5 \times 10^{-3} \text{ sec}^{-1}$,



is possible, and a working value such as

$$10^{-3} \leq a_9 \equiv J_{\text{HO}_2} \leq 10^{-4} \text{ sec}^{-1} \quad (39b)$$

may be considered. It is almost certain that the photodissociation process is less important than reaction (37) above 30 km in the stratosphere and in the whole mesosphere.

As for the photodissociation process



in which the bonds between H and O atoms are difficult to break, it can be ignored and $a_{10} = 0$.

Expressions for the equilibrium ratios of $n(\text{OH})/n(\text{H})$ and $n(\text{HO}_2)/n(\text{H})$ can be easily obtained if it is assumed, as a first approximation, that only (30) to (40) are involved. Thus, if reactions with rate coefficients $a = 0$ are ignored,

$$\frac{n(\text{OH})}{n(\text{H})} = \frac{[a_1 n(\text{M}) n(\text{O}_2) + a_3 n(\text{O}_3)] [a_7 n(\text{O}) + J_{\text{HO}_2}] + a_7 n(\text{O}) a_2 n(\text{O}_3)}{a_5 n(\text{O}) [a_7 n(\text{O}) + J_{\text{HO}_2}]} \quad (41a)$$

In this equation $a_3 n(\text{O}_3) < a_1 n(\text{M}) n(\text{O}_2)$; in the atmospheric region where $a_7 n(\text{O}) > J_{\text{HO}_2}$, (41a) becomes

$$\frac{n(\text{OH})}{n(\text{H})} = \frac{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)}{a_5 n(\text{O})} \quad (41b)$$

which is the simple expression for the ratio of $n(\text{OH})/n(\text{H})$ in the whole mesosphere.

In the same way the expression for the equilibrium ratio of $n(\text{HO}_2)/n(\text{H})$ is obtained

$$\frac{n(\text{HO}_2)}{n(\text{H})} = \frac{a_1 n(\text{M}) n(\text{O}_2) + a_3 n(\text{O}_3)}{a_7 n(\text{O}) + J_{\text{HO}_2}} + \frac{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)}{a_7 n(\text{O}) + J_{\text{HO}_2}} \times \frac{a_6 n(\text{O}_3)}{a_5 n(\text{O})} \quad (41c)$$

and, where $a_7 n(O) > J_{HO_2}$ and $a_3 n(O_3) < a_1 n(M) n(O_2)$

$$\frac{n(HO_2)}{n(H)} = \frac{a_1 n(M) n(O_2)}{a_7 n(O)} + \frac{a_6 n(O_3)}{a_5 n(O)} \times \frac{a_1 n(M) n(O_2) + a_2 n(O_3)}{a_7 n(O)} \quad (41d)$$

Expressions (41b) and (41d), assuming $a_5 = a_7$, lead to

$$\frac{n(HO_2)}{n(OH)} = \frac{a_1 n(M) n(O_2)}{a_1 n(M) n(O_2) + a_2 n(O_3)} + \frac{a_6 n(O_3)}{a_7 n(O)} \quad (41e)$$

which can be accepted where $a_7 n(O) > J_{HO_2}$.

Numerical values show that

$$\frac{n(HO_2)}{n(OH)} = \frac{a_1 n(M) n(O_2)}{a_1 n(M) n(O_2) + a_2 n(O_3)} \quad (41f)$$

is a sufficient approximation in the lower thermosphere and mesosphere.

In the stratosphere, the term $a_6 n(O_3)/a_7 n(O)$ should play a role. In the same way

$$\frac{n(HO_2)}{n(H)} = \frac{a_1 n(M) n(O_2)}{a_7 n(O)} \quad (41g)$$

is the practical ratio in the whole mesosphere. Numerical values are given in Table IV. The essential result is that the atomic hydrogen concentration is greater than the hydroxyl and hydroperoxyl concentrations in the upper mesosphere. The ratio of $n(HO_2)/n(OH)$, which is about 0.8, indicates that both radicals have almost the same concentrations in the whole of the mesosphere.

TABLE IV.- Hydroxyl and hydroperoxyl radicals in the mesosphere
Overhead sun conditions.

Altitude	$n(\text{OH})/n(\text{H})$	$n(\text{HO}_2)/n(\text{H})$	$n(\text{HO}_2)/n(\text{OH})$
85	4.5×10^{-3}	2.8×10^{-3}	0.63
80	2.6×10^{-2}	2.1×10^{-2}	0.81
75	2.9×10^{-1}	2.5×10^{-1}	0.86
70	8.3×10^{-1}	7.0×10^{-1}	0.85
65	1.8×10^0	1.4×10^0	0.82
60	3.5×10^0	2.7×10^0	0.78
55	6.7×10^0	4.9×10^0	0.73
50	2.9×10^1	2.3×10^1	0.79

When hydrogen compounds are considered, the differential equation (23) relating to atomic oxygen becomes

$$\frac{dn(O)}{dt} + 2k_1 n(M) n^2(O) + [k_2 n(M) n(O_2) + k_3 n(O_3) + a_5 n(OH) + a_7 n(HO_2)] n(O) = 2n(O_2) J_2 + n(O_3) J_3 \quad (42)$$

where the reactions with the a coefficients are the additional processes in which atomic oxygen is involved in a hydrogen-oxygen atmosphere. From this equation, one sees that oxygen atoms may disappear by reaction with OH and HO₂. Since $a_5 \simeq a_7 \simeq 4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, a direct effect is not important at low altitudes where the term $k_2 n(M) n(O_2)$ (see Table II) reaches its highest values. However, in the mesosphere and particularly in its upper part, it is clear that $k_2 n(M) n(O_2)$ can be less than $a_5 n(OH) + a_7 n(HO_2)$.

Instead of (26a), for the upper mesosphere and lower thermosphere we must write

$$\frac{n(O_3)}{n(O)} = \frac{k_2 n(M) n(O_2)}{J_3 + k_3 n(O) + a_2 n(H)} \equiv \frac{k_2 n(M) n(O_2)}{J_{3a}} \quad (43)$$

with $J_{3a} = J_3 + k_3 n(O) + a_2 n(H) \simeq J_3 + a_2 n(H)$ (44)

By introducing (43) into (42), the variation of atomic oxygen is given by

$$\begin{aligned} \frac{dn(O)}{dt} + 2n^2(O) \left[k_1 n(M) + \frac{k_3 k_2 n(M) n(O_2)}{J_{3a}} \right] \\ + n(O) \left[a_2 n(H) \frac{k_2 n(M) n(O_2)}{J_{3a}} + a_5 n(OH) + a_7 n(HO_2) \right] = 2 n(O_2) J_2 \end{aligned} \quad (45)$$

Such an equation corresponds to photochemical conditions in the lower thermosphere and in the mesosphere. Numerical calculations near the mesopause level show (see Table II) that

$$k_1 n(M) = 1 \times 10^{-18} \text{ cm}^3 \text{ sec}^{-1} \simeq k_3 k_2 n(M) n(O_2) / J_3 \quad (46)$$

at 80 km ; i.e. that the direct recombination rate of oxygen atoms is of the same order of magnitude as their association rate to form ozone. However, such rate coefficients are too small (see equation 29) to lead to photochemical equilibrium conditions. As far as the term involving H, OH and HO₂ is concerned, the effect is also too small in the thermosphere and chemical equilibrium cannot be reached for atomic oxygen. Its vertical distribution in the lower thermosphere is subject to the transport conditions controlled by eddy diffusion.

In such conditions, if we adopt the conventional value $n(H) = 3 \times 10^7 \text{ cm}^{-3}$ at 100 km corresponding to

$$n(H) = n(N_2) / 2 \times 10^5 \text{ cm}^{-3} \quad (47)$$

with the hypothesis that atomic hydrogen in the lower thermosphere is practically uniformly mixed, its concentration reaches $7 \times 10^8 \text{ cm}^{-3}$ at the mesopause (see Table V). A possible approximation for equation (45) is

$$\begin{aligned} \frac{dn(O)}{dt} + \left[a_2 n(H) \frac{k_2 n(M) n(O_2)}{J_{3a}} + a_5 n(OH) + a_7 n(HO_2) \right] n(O) \\ = 2 n(O_2) J_2 \end{aligned} \quad (48)$$

or even

$$\frac{dn(O)}{dt} + \left[a_2 n(H) \frac{k_2 n(M) n(O_2)}{J_3 + a_2 n(H)} \right] n(O) = 2n(O_2) J_2 \quad (49)$$

TABLE V.- Adopted parameters in the lower thermosphere (overhead sun conditions).

Altitude (km)	n(O) (cm ⁻³)	n(H) (cm ⁻³)	n(O ₃) (cm ⁻³)	n[O(¹ D)] (cm ⁻³)
120	1.0x10 ¹¹	4x10 ⁶	6.0x10 ²	5.1x10 ³
115	1.5x10 ¹¹	6x10 ⁶	4.0x10 ³	5.1x10 ³
110	2.3x10 ¹¹	9x10 ⁶	2.7x10 ⁴	4.1x10 ³
105	2.9x10 ¹¹	1.5x10 ⁷	2.0x10 ⁵	2.2x10 ³
100	3.2x10 ¹¹	3.5x10 ⁷	1.6x10 ⁶	1.2x10 ³
95	3.3x10 ¹¹	8.7x10 ⁷	1.3x10 ⁷	5.0x10 ²
90	3.0x10 ¹¹	2.3x10 ⁸	1.1x10 ⁸	4.2x10 ²
85	3.0x10 ¹⁰	6.9x10 ⁸	1.0x10 ⁸	1.2x10 ²

at the mesopause. With the following time τ_0

$$\tau_0 = \frac{J_3 + a_2 n(H)}{2a_2 n(H) k_2 n(M) n(O_2)} \quad (50)$$

necessary to reach a sufficient fraction of the equilibrium value, it is found that τ_0 at 85 km is only 8.4×10^3 sec. Thus, when atomic hydrogen plays a role at the mesopause level, an equilibrium value of $n(O)$ can be reached in about two hours. Adopting all the numerical parameters used here, and for an overhead sun,

$$n(O)_{85 \text{ km}} \simeq 3 \times 10^{10} \text{ cm}^{-3} \quad (51)$$

and, with (49) and (44)

$$n(O_3)_{85 \text{ km}} \simeq 10^8 \text{ cm}^{-3} \quad (52)$$

In the lower thermosphere there is a transition region where the atomic oxygen concentration must increase rapidly since at 90 km the time to reach photoequilibrium is not less than 10^5 sec.

After sunset, in the lower thermosphere,

$$\frac{dn(O_3)}{dt} + n(O_3) a_2 n(H) = k_2 n(M) n(O_2) n(O) \quad (53)$$

Provided $n(O)$ does not vary appreciably, the relevant solution to the differential equation (53) is simply

$$n(O_3) = n(O_3)_{t=0} e^{-a_2 n(H) t} + \frac{k_2 n(M) n(O_2) n(O)}{a_2 n(H)} \left[1 - e^{-a_2 n(H) t} \right]$$

(54)

Since $a_2 n(H) t = 1$ after less than 100 sec at 100 km, the ozone concentration can be conveniently written in the nighttime thermosphere as

$$n(O_3) = \frac{k_2 n(M) n(O_2) n(O)}{a_2 n(H)} \quad (55)$$

while the daytime value is

$$n(O_3) = \frac{k_2 n(M) n(O_2) n(O)}{a_2 n(H) + J_3} \quad (56)$$

The Bates-Nicolet process (32) which leads to the OH airglow spectrum occurs in the lower thermosphere according to, (56),

$$\frac{dn(OH^*)}{dt} \underset{v'' \leq 9}{=} a_2 n(H) n(O_3) = a_2 n(H) \frac{k_2 n(M) n(O_2) n(O)}{J_3 + a_2 n(H)} \quad (57)$$

or for nighttime conditions, (55),

$$\frac{dn(OH^*)}{dt} = k_2 n(M) n(O_2) n(O) = + \frac{dn(O_3)}{dt} \quad (58)$$

which corresponds to the ozone formation. Thus, in the lower thermosphere, the number of excited molecules OH^* which are produced is almost $10^7 \text{ cm}^{-3} \text{ sec}^{-1}$, i.e. a total production which is not less than $5 \times 10^{12} \text{ OH}^*$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$.

In the region where atomic oxygen is in photochemical equilibrium, the conventional stratospheric equation

$$\frac{dn(O_3)}{dt} + 2 n^2(O_3) \frac{J_3 k_3}{k_2 n(M) n(O_2)} = 2 n(O_2) J_2 \quad (59)$$

indicates that photochemical equilibrium values can be reached even in the upper stratosphere. Below 35 km, the times required become too long and departures from equilibrium conditions are observed. However, (59) must be replaced in a hydrogen-oxygen atmosphere by

$$\begin{aligned} & \frac{dn(O_3)}{dt} + 2 n^2(O_3) \frac{J_3 k_3}{k_2 n(M) n(O_2)} + n(O_3) a_2 n(H) + \\ & n(O_3) \left\{ \left[\frac{a_5 J_3}{k_2 n(M) n(O_2)} + a_6 \right] n(OH) + \left[\frac{a_7 J_3}{k_2 n(M) n(O_2)} + a_{6c} \right] n(HO_2) \right\} \\ & = 2n(O_2) J_2 \end{aligned} \quad (60)$$

in which the effect of H, OH and HO₂ reactions is represented by the symbol a from reactions (32), (35), (36) and (37). If (60) is compared with (59), it is clear that the effect of hydrogen compounds is equivalent to an increase of the photodissociation coefficient J₃. In other words, the ozone dissociation is increased by additional processes involving oxygen atoms so that the equivalent O₃ photodissociation coefficient is written

$$J_{3A} = J_3 [1 + A] \quad (61)$$

where A is given by

$$\begin{aligned} A = & \frac{a_2 n(H) k_2 n(M) n(O_2)}{2 J_3 k_3 n(O_3)} + \frac{a_5 n(OH)}{2 k_3 n(O_3)} \left[1 + \frac{a_6}{a_5} \cdot \frac{k_2 n(M) n(O_2)}{J_3} \right] + \\ & \frac{a_7 n(HO_2)}{2 k_3 n(O_3)} \left[1 + \frac{a_{6c}}{a_5} \frac{k_2 n(M) n(O_2)}{J_3} \right] \end{aligned} \quad (62)$$

Using (60) and (61), the conventional equation for equilibrium conditions in the stratosphere is replaced by

$$n(O_3) = \left[\frac{k_2}{k_3} n(M) n^2(O_2) \frac{J_2}{J_3 (1 + A)} \right]^{1/2} \quad (63)$$

The correction term $(1 + A)^{1/2}$ in the stratosphere where $n(H)$ is negligible, and when a_6 is neglected and $a_7 = a_5$, can be written

$$[1 + A]^{1/2} = \left[1 + \frac{a_7 \{n(OH) + n(HO_2)\}}{2k_3 n(O_3)} \right]^{1/2} \quad (64)$$

It can be shown that a very high mixing ratio $n(H_2O)/n(M)$ is required in order to have an important effect on the ozone concentration in the stratosphere. For example, a mixing ratio $n(H_2O)/n(M) = 6.5 \times 10^{-6}$ leads to a value $[1 + A]^{1/2} = 1.5$ in the stratosphere. Such a modification is only important from a theoretical point of view. It seems that almost impossibly high mixing ratios (5×10^{-5} , 10^{-4}) would be required in order to affect in any significant way the ozone concentration in the lower stratosphere.

In the mesosphere there is an important difference between a pure oxygen atmosphere and a hydrogen-oxygen atmosphere. The correction term which applies in the mesosphere

$$[1 + A]^{1/2} = \left[1 + \frac{a_2 n(H) k_2 n(M) n(O_2)/J_3 + a_5 n(OH) + a_7 n(HO_2)}{2 k_3 n(O_3)} \right]^{1/2} \quad (65)$$

increases to about 100 at the mesopause if it is 1.5 at the stratopause. There is a considerable decrease in the atomic oxygen concentration and consequently a parallel decrease in the ozone concentration, Fig. 9 illustrates that difference between an oxygen mesosphere and a hydrogen-oxygen mesosphere.

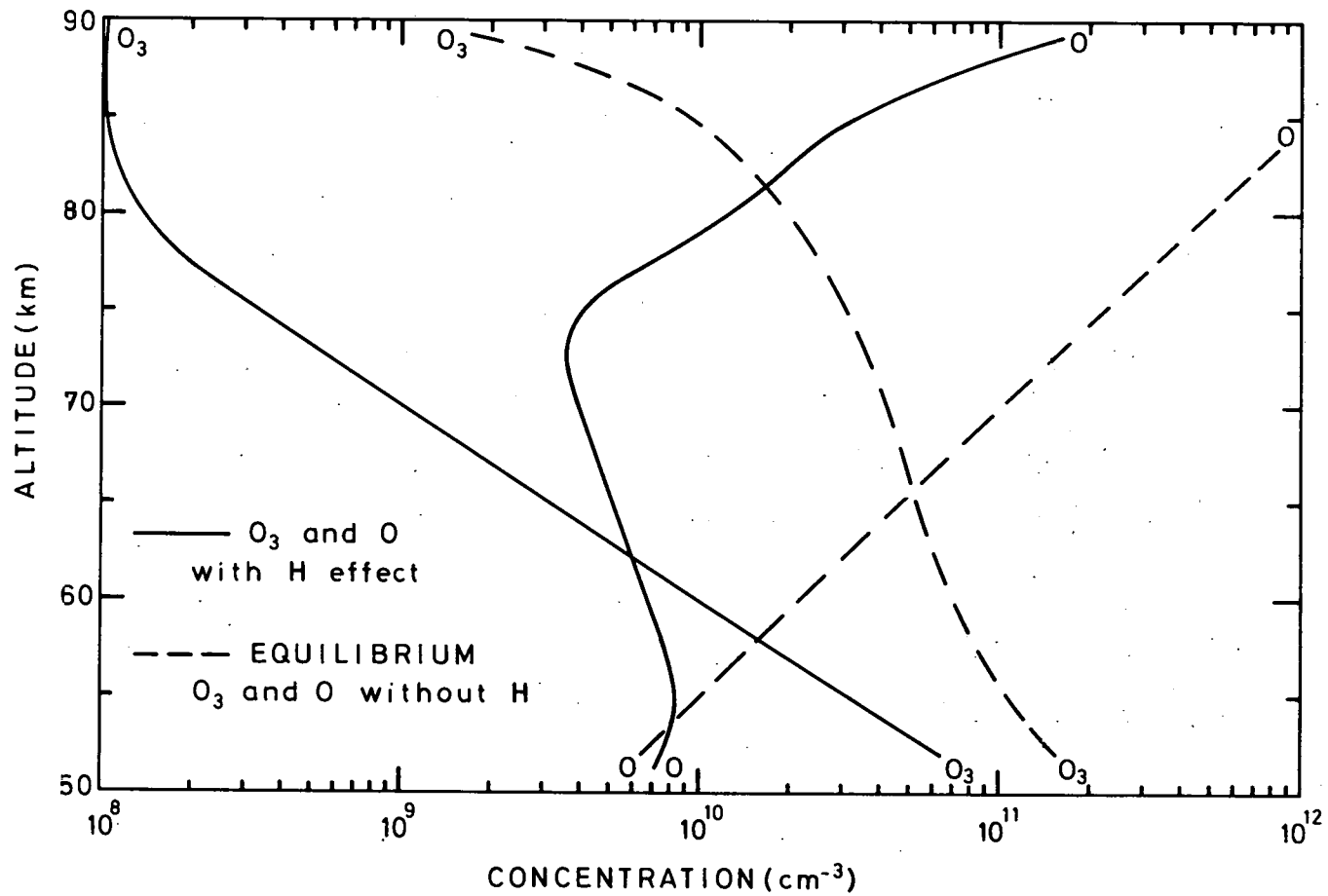


Fig. 9.- Equilibrium conditions in the mesosphere of ozone and atomic oxygen in a pure oxygen-nitrogen atmosphere and in an atmosphere where hydrogen is involved.

In the thermosphere atomic hydrogen is the most important hydrogen constituent, $n(\text{H})/n(\text{OH}) > 1$ and $n(\text{H})/n(\text{HO}_2) > 1$, and its vertical distribution (Table V) has been assumed to be a mixing distribution. Atomic oxygen concentrations are also fixed according to arbitrary eddy diffusion coefficients. Dynamic effects acting on the vertical distribution of atomic oxygen will modify the ozone distribution in the lower thermosphere. Below the mesopause, 85 to 80 km, the aeronomic conditions are such that they correspond to a transition region between mixing and photochemical equilibrium. In the mesosphere, therefore, it is necessary to determine the production of hydroxyl and hydroperoxyl radicals.

V. METHANE IN THE STRATOSPHERE AND MESOSPHERE

Methane which has been found as a permanent constituent of the troposphere has continuous sources at ground level. Its total amount by volume is 1.5×10^{-6} of the major gases N_2 and O_2 . Methane can be dissociated by ultraviolet radiation. However, since the absorption cross-section is very small at $\lambda > 1500 \text{ \AA}$, the aeronomic photodissociation of CH_4 arises principally from Lyman- α with a photodissociation coefficient at zero optical depth

$$J_{\text{CH}_4}(\lambda = 1216 \text{ \AA}) = 5 \times 10^{-6} \text{ sec}^{-1} \quad (66a)$$

The total photodissociation coefficient is

$$J_{\text{CH}_4} = 7 \times 10^{-6} \text{ sec}^{-1} \quad (66b)$$

and it must be considered only above 100 km. Thus, the photodissociation coefficient of CH_4 is a decreasing function of the optical depth in the mesosphere and is negligible in the lower mesosphere (Fig. 10). The photolysis of CH_4 due to Lyman- α may be represented by (see a discussion by Strobel, 1969)

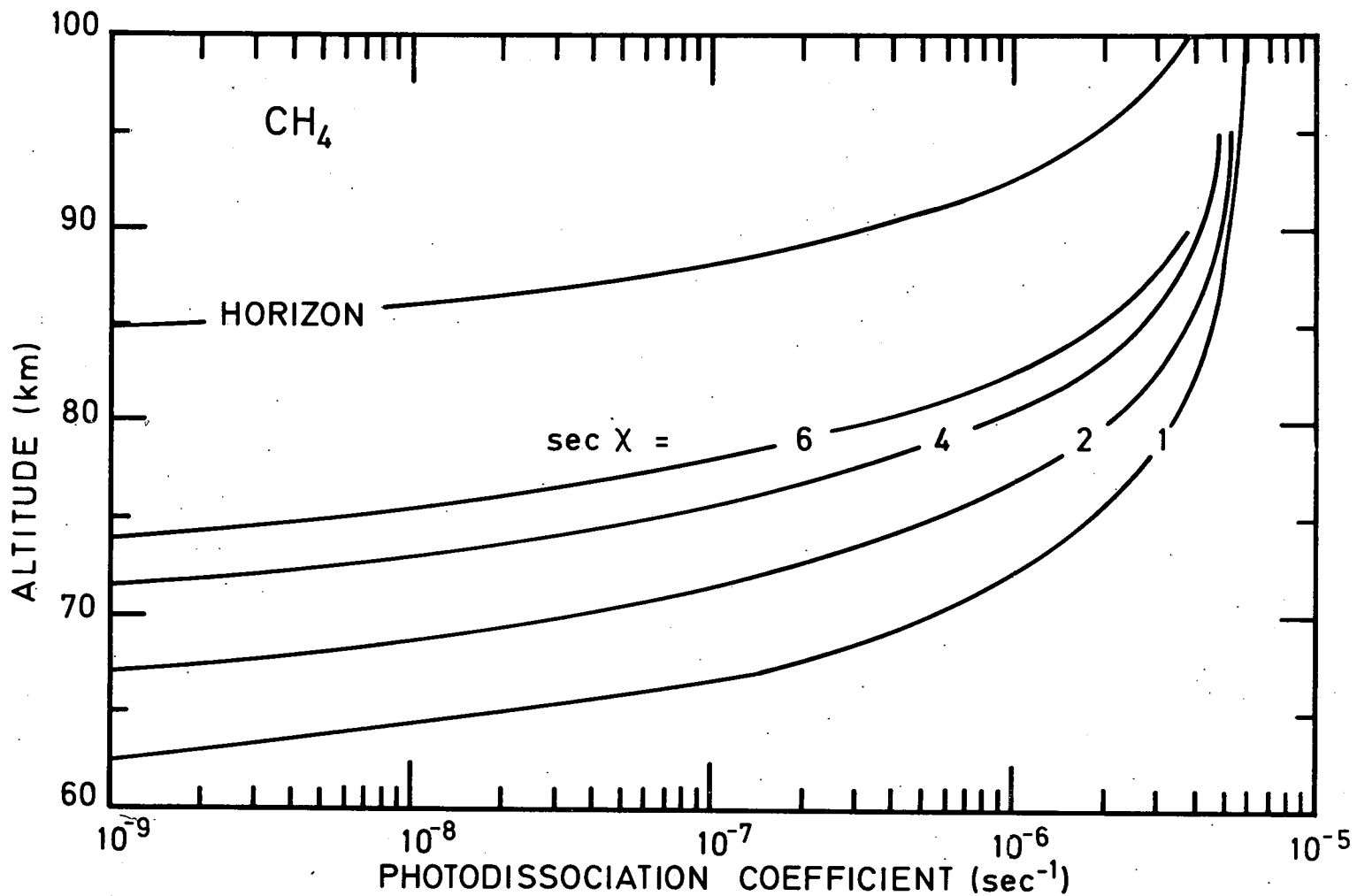
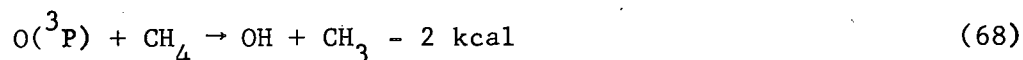


Fig. 10.- Photodissociation coefficient of methane for various solar zenith angles. From overhead sun conditions, $\chi = 0$, to $\chi = 90^\circ$, horizon.



But photodissociation is not the only disruptive process of CH_4 . The oxidation of methane according to



being endothermic by about 2 kcal, is a slow reaction. Its activation energy is not less than 7 kcal, according to various laboratory measurements [see for example, Brown and Thrush, 1967 ; Westenberg and de Haas, 1969 ; Wong and Potter, 1967]. Adopting the minimum activation energy, the rate coefficient is written

$$a_{\text{CH}_4-\text{O}} = 3.5 \times 10^{-13} T^{1/2} e^{-3650/T} \text{ cm}^3 \text{ sec}^{-1} \quad (69)$$

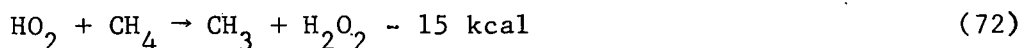
Other oxidation processes may be considered ; with OH the following reaction is possible



This reaction according to recent laboratory measurements [Greiner, 1970] has a rate coefficient which can be written

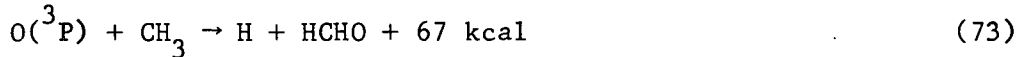
$$a_{\text{OH}-\text{CH}_4} = 1.8 \times 10^{-13} T^{1/2} e^{-1750/T} \text{ cm}^3 \text{ sec}^{-1} \quad (71)$$

A reaction such as



is endothermic by about 15 kcal and it is difficult to see how hydroperoxyl radicals could be responsible for an attack on methane.

When the methyl radical CH_3 is produced, i.e. when the removal of a single hydrogen atom from a methane molecule takes place, it is certain that there is a permanent destruction of that molecule. The following reaction

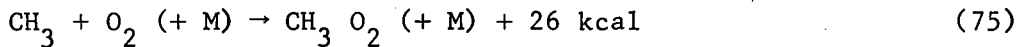


yielding formaldehyde the [Niki et al, 1968] can be considered as the most important process since its rate coefficient is not less than $3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K. Reaction (73) may be followed by $\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH}$ and can end by $\text{O} + \text{HCO} \rightarrow \text{OH} + \text{CO} + 84 \text{ kcal}$.

Methyl radicals react also with ozone and molecular oxygen



and

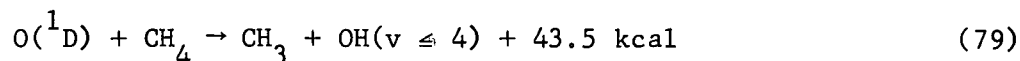


If we consider that atomic oxygen can be in the electronically excited ${}^1\text{D}$ state, the reaction $\text{O}({}^1\text{D}) + \text{CH}_4$ is possible [Cadle, 1964] with no activation energy [DeMore and Raper, 1967]. It proceeds by the three paths



which, from an aeronomic point of view, correspond to a dissociation process of CH_4 . As (78) seems to be the most important reaction [DeMore

and Raper, 1967], we conclude that



with the following working value for the rate coefficient

$$a_{CH_4-O^*}^* = 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (80)$$

Such a reaction will play a role in a sunlit atmosphere where the ozone photodissociation is important, i.e in the stratosphere and lower mesosphere. A reaction such as



cannot be important since the quenching rate coefficient, which is about $5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ [Filseth et al, 1970] at 298°K, is too small.

From the foregoing discussion it is apparent that the mechanisms responsible for the dissociation of CH_4 can be identified with an oxidation process by $O(^1D)$ atoms throughout the stratosphere, by $O(^3P)$ atoms near the stratopause level and by photodissociation by Lyman- α in the mesosphere.

Using the numerical values of $O(^1D)$ and $O(^3P)$ atom which are given in Table III for overhead sun conditions, the dissociation of CH_4 can be determined and is particularly important near the stratopause level. With a mixing distribution such as it is indicated in Table VI, the average diffusion flow which would be required at the stratosphere should be

$$F_{50 \text{ km}}(CH_4) > 10^9 \text{ cm}^2 \text{ sec}^{-1} \quad (82)$$

Under mixing conditions, the average molecular diffusion flow F_D in the stratosphere is

TABLE VI.- Dissociation of CH₄ under mixing conditions in the stratosphere
for an overhead sun

Altitude (km)	Concentration (cm ⁻³)	O(¹ D) oxidation (cm ⁻³ sec ⁻¹)	O(¹ D) oxidation (cm ⁻² sec ⁻¹)	Eddy diffusion coefficient (cm ⁻² sec ⁻¹)
15	5.8x10 ¹²	5.3x10 ¹	-	1.4x10 ¹
20	2.6x10 ¹²	2.3x10 ²	8.0x10 ⁷	1.5x10 ²
25	1.2x10 ¹²	5.7x10 ²	2.9x10 ⁸	8.9x10 ²
30	5.3x10 ¹¹	1.3x10 ³	7.7x10 ⁸	4.8x10 ³
35	2.5x10 ¹¹	2.5x10 ³	1.8x10 ⁹	2.3x10 ⁴
40	1.2x10 ¹¹	4.0x10 ³	3.9x10 ⁹	8.3x10 ⁴
45	6.4x10 ¹⁰	3.9x10 ³	5.5x10 ⁹	1.6x10 ⁵
50	3.5x10 ¹⁰	2.1x10 ³	6.9x10 ⁹	1.6x10 ⁵

$$F_D(\text{CH}_4) = 7 \times 10^6 \text{ cm}^2 \text{ sec}^{-1} \quad (83)$$

which is a negligible fraction of the possible loss by an oxydation process. Since the tropospheric mixing time is short enough to lead to an uniform distribution of CH_4 in the whole troposphere, the injection rate of CH_4 into the stratosphere is the essential process which must be considered. In other words, the conditions of the tropopause must determine the behavior of the stratospheric CH_4 . Assuming that the CH_4 is injected with no restriction into the stratosphere, it is possible to determine the conditions which are required to maintain a certain vertical distribution of a constituent which is continuously lost such as CH_4 .

The vertical diffusive speed w_D of a minor constituent of mass m_1 and concentration n_1 relative to the general mass m is of the form [see, for example Nicolet, 1968]

$$w_D = - D_{12} \left[\frac{1}{n_1} \frac{\partial n_1}{\partial r} + \frac{m_1}{mH} + \frac{1}{T} \frac{\partial T}{\partial r} \right] \quad (84)$$

where D_{12} is the coefficient of molecular diffusion. H is the atmospheric scale height

$$H = \frac{k T}{mg} \quad (85)$$

where k is the Boltzmann constant, T is the temperature and g denotes the gravitational acceleration. The properties of the gas are taken to vary in only one direction, namely along the Earth's radius ; r is the geocentric altitude.

Since the differentiation of the gas law in the form $p = n k T$, where p and n denote the total pressure and total concentration respectively, leads to

$$\frac{dp}{p} = \frac{dn}{n} + \frac{dT}{T} = -\frac{dr}{H}, \quad (86)$$

if the static law $dp = -g n m dr$ is used, it is possible to use the scale height \mathcal{H}_1 for the constituent of mass m_1 defined by

$$\frac{dp_1}{p_1} = \frac{dn_1}{n_1} + \frac{dT}{T} = -\frac{dr}{\mathcal{H}_1} \quad (87)$$

With (87) the formula (84) for molecular diffusion becomes

$$w_D = \frac{D_{12}}{H} \left[\frac{H}{\mathcal{H}_1} - \frac{m_1}{m} \right]. \quad (88)$$

When eddy diffusion is involved, the vertical speed is defined by

$$w_{\mathcal{D}} = \frac{\mathcal{D}_{12}}{H} \left[\frac{H}{\mathcal{H}_1} - 1 \right] \quad (89)$$

where \mathcal{D}_{12} is the eddy diffusion coefficient.

Since the coefficient of molecular diffusion in the stratosphere is

$$2 \text{ cm}^2 \text{ sec}^{-1} \leq D_{\text{CH}_4} \leq 4 \times 10^2 \text{ cm}^2 \text{ sec}^{-1} \quad (90)$$

it is clear that eddy diffusion must be involved in order to maintain CH_4 in the stratosphere. Considering that the methane which is destroyed chemically in a sunlit atmosphere by reaction with $\text{O}({}^1\text{D})$ oxygen atoms is given approximately by

$$F_{\text{CH}_4} = \frac{1}{2} a^*_{\text{O}^*-\text{CH}_4} n(\text{O}({}^1\text{D})) n(\text{CH}_4) H(\text{CH}_4) \text{ cm}^2 \text{ sec}^{-1} \quad (91)$$

and since the loss must correspond to the diffuse upward current of CH_4 molecules by eddy diffusion

$$F_{\text{CH}_4} = n(\text{CH}_4) w_{\text{CH}_4} = \frac{n(\text{CH}_4) \mathcal{D}_{12}}{H} \left[\frac{H}{H_1} - 1 \right] \text{cm}^2 \text{sec}^{-1}, \quad (92)$$

it is possible to determine for a certain ratio H_{CH_4}/H , the eddy coefficient \mathcal{D}_{12} which is required. With $H_{\text{CH}_4} = 0.9 H$, in order to indicate a small departure from mixing conditions, and $H_{\text{CH}_4} = 0.5 H$, to show that there is a definite decrease in the mixing ratio in the stratosphere, the following expressions are obtained :

$$\mathcal{D}_{12}(0.9H) = 4 a^* n^* H^2 \quad (93)$$

if $H_{\text{CH}_4} = 0.9 H$, and

$$\mathcal{D}_{12}(H/2) = a^* n^* H^2/4 \quad (94)$$

if $H_{\text{CH}_4} = H/2$. Results are given in Table VI and are also illustrated in Fig. 11. An eddy diffusion coefficient greater than $10^5 \text{ cm}^2 \text{sec}^{-1}$ would be required in the upper stratosphere in order to maintain an approximately constant volume ratio of $n(\text{CH}_4)/n(\text{M})$. Even for a scale height $H_{\text{CH}_4} = \frac{1}{2} H(\text{M})$, an eddy diffusion coefficient not less than $10^4 \text{ cm}^2 \text{sec}^{-1}$ is required below the stratopause. It seems, therefore, that it is not possible to maintain a constant mixing ratio of methane in the stratosphere. Recent observations [Bainbridge and Heidt, 1966 ; Scholz et al, 1970] show that there is a decrease of the CH_4 mixing ratio in the stratosphere and, therefore, that the eddy diffusion coefficient in the upper stratosphere is certainly less than $10^4 \text{ cm}^2 \text{sec}^{-1}$. Thus, the oxidation of the stratospheric methane leads to a continuous production of stratospheric water vapor with the formation of CO and CO_2 . Further measurements of the stratospheric CH_4 distribution are needed to determine the scale height of CH_4 in the stratosphere and, therefore, to provide information on its injection from the troposphere

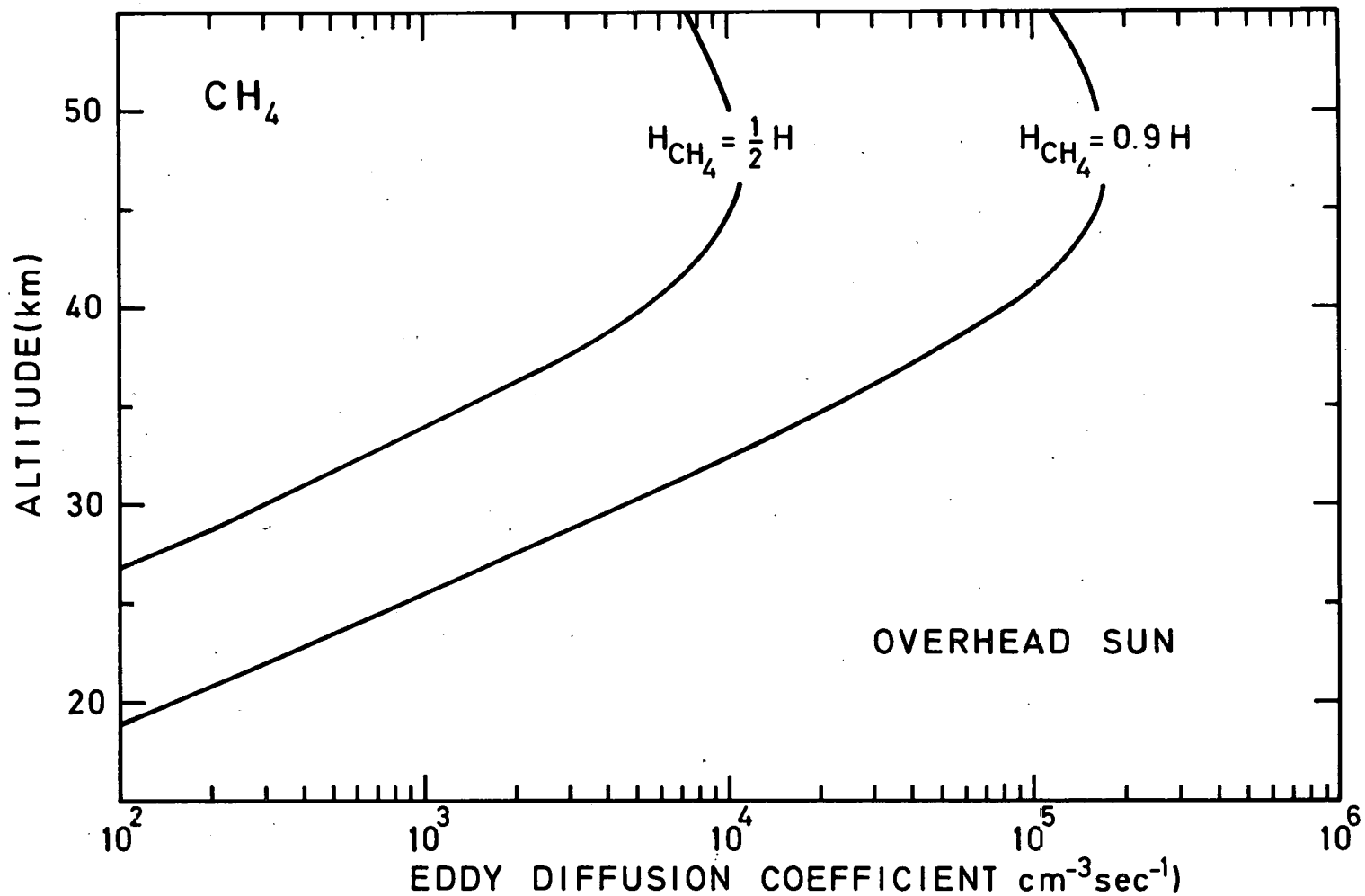


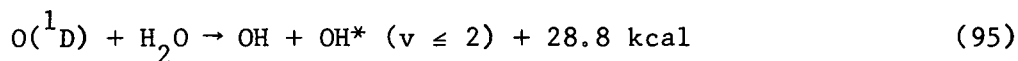
Fig. 11.- Eddy diffusion coefficient which would be required in the stratosphere to maintain a vertical distribution of CH₄ with a scale height H_{CH_4} corresponding to 0.5 of the atmospheric scale height H, and corresponding to 0.9 of H, i.e. almost mixing conditions.

into the stratosphere and on the upward diffuse current resulting from eddy diffusion. Finally, since the oxidation of methane in the stratosphere is a very important process, its presence in the mesosphere will not be sufficient to permit it to play a leading role in the various reactions in which hydrogen compounds are involved.

VI. WATER VAPOR IN THE STRATOSPHERE AND MESOSPHERE

The water vapor content is very small in the stratosphere ; 3×10^{-6} is not an unreasonable value to adopt for the order of magnitude of the fractional volume concentration of water vapor [Williamson and Houghton, 1965 ; Mastenbrook, 1968 ; Sissenwine et al, 1968 ; McKinnon and Morewood, 1970]. Since the amount of methane by volume is 1.5×10^{-6} and that of molecular hydrogen is not far from 0.5×10^{-6} , the total amount of hydrogen atoms cannot be far from 10^{-5} above the tropopause or the equivalent H_2O amount should correspond to 6.5×10^{-6} .

An effect caused by oxygen atoms in their normal state 3P on H_2O has not been detected since the reaction is endothermic, but atoms in their first excited state 1D leads to [Engleman, 1965].



for which the following round figure for the rate coefficient is adopted

$$a_{H_2O}^* = 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (96)$$

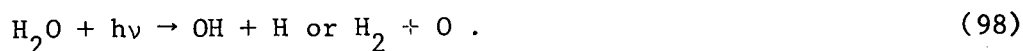
while the possible variation is $(1 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. With the $O(^1D)$ concentrations which are used here (Table III), it is clear that there is permanent destruction of H_2O in the stratosphere. The dissociation rate coefficient is of the order $10^{-10} \text{ sec}^{-1}$ in the lower stratosphere (see

Fig. 12) for overhead sun conditions and reaches a maximum of more than $5 \times 10^{-8} \text{ sec}^{-1}$ near the stratopause.

Water vapor can be dissociated by sunlight and its photodissociation coefficient for zero optical depth is

$$J_{\text{H}_2\text{O}} = 10^{-5} \text{ sec}^{-1} \quad (97)$$

corresponding to



The photodissociation in the upper mesosphere is due mainly to the effect of Lyman- α , and the effect of the spectral range of the Schumann-Runge bands plays the leading role in the lower mesosphere. The result of the calculation of the photodissociation is given in Fig. 13 for overhead sun conditions. The photodissociation rate coefficient decreases in the mesosphere by a factor of the order of 1000, since at 50 km it reaches about

$$J_{\text{H}_2\text{O}}(50 \text{ km}) \simeq 10^{-8} \text{ sec}^{-1} . \quad (99)$$

In the stratosphere, the photodissociation process is less important than the oxidation process (see Fig. 12) due to excited oxygen atoms $\text{O}(^1\text{D})$. As before, the effect of $\text{O}(^1\text{S})$ atoms is considered negligible since their production rate is too small compared with other production processes.

It must be pointed out that the photodissociation process which corresponds to Lyman- α leads to a dissociation coefficient J_{H_2} for zero optical depth

$$J_{\text{H}_2}(\text{L } \alpha) = 4.3 \times 10^{-6} \text{ sec}^{-1} \quad (100a)$$

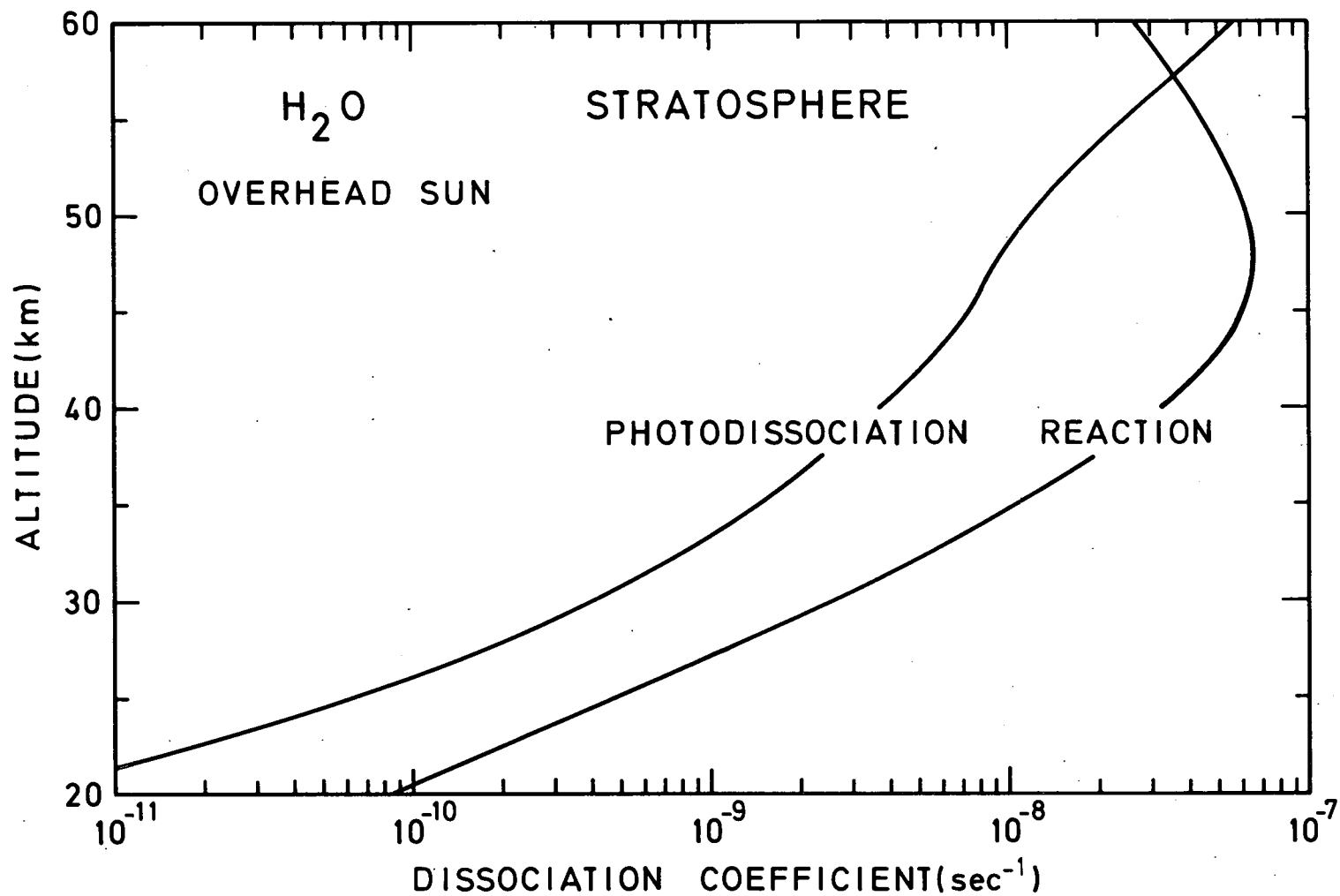


Fig. 12.- Dissociation coefficient of the water vapor in the stratosphere. The effect of the reaction of H₂O with O(¹D) is more important than the direct photodissociation.

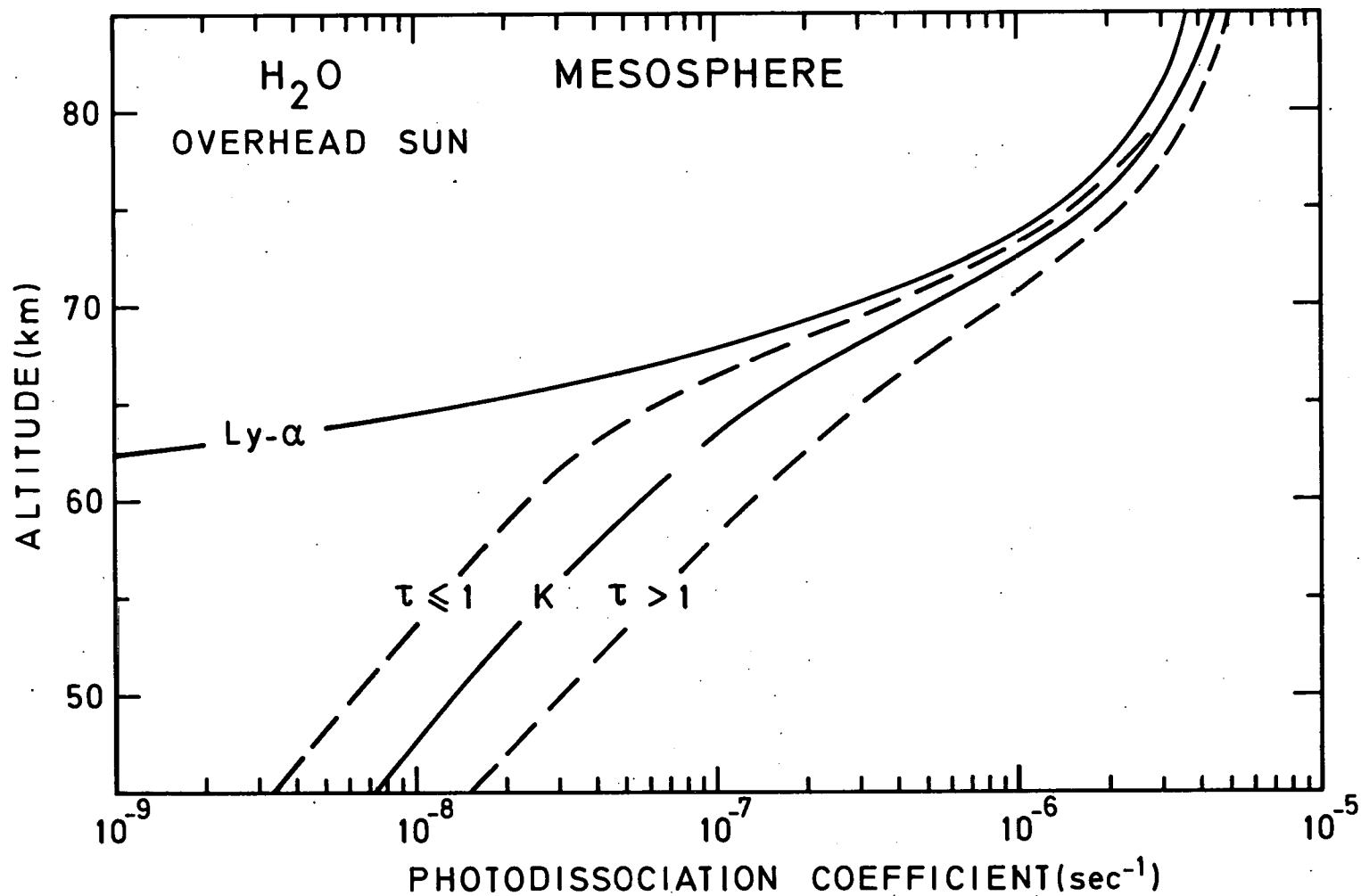


Fig. 13.- Photodissociation coefficient of H_2O in the mesosphere. In the upper part of the mesosphere, Lyman- α (curve Ly- α) plays the principal role. In the lower part the dissociation comes from the solar radiation of the spectral region involving the Schumann-Runge bands.

which is identical to the photodissociation coefficient in the Schumann-Runge continuum

$$J_{\text{H}_2\text{O}}(\text{SRC}) = 4.3 \times 10^{-6} \text{ sec}^{-1} \quad (100b)$$

The values in the O_2 Schumann-Runge bands region and in the O_2 Herzberg continuum are respectively,

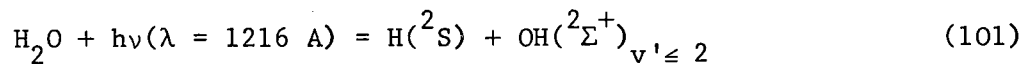
$$J_{\text{H}_2\text{O}}(\text{SRB}) = 1.5 \times 10^{-6} \text{ sec}^{-1} \quad (100c)$$

and

$$J_{\text{H}_2\text{O}}(\text{HER}) = 1.2 \times 10^{-9} \text{ sec}^{-1} \quad (100d)$$

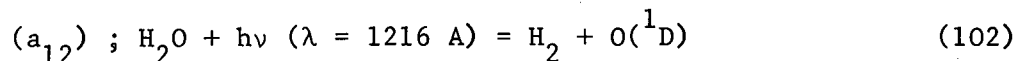
Since the H_2O photodissociation in the lower mesosphere depends on its absorption in the Schumann-Runge bands region, the optical depth is related to the band structure. In figure 13, the results of the exact computation with the detailed rotational structure and the data obtained with mean coefficients adapted to $\tau \leq 1$ and $\tau \geq 1$ show that an error of a factor of 2 is involved even when appropriate constant cross-sections for the absorption of molecular oxygen are used.

At the mesopause level, the photodissociation of H_2O by Lyman- α is the most important process. At 1216 A the following process occurs

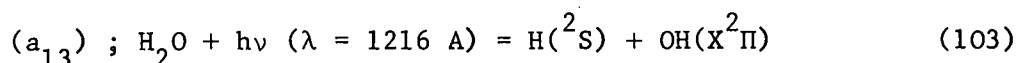


where OH is in the electronically excited state $^2\Sigma^+$ leading to a fluorescence process corresponding to several percent of the total dissociation [Carrington, 1964].

Direct production of molecular hydrogen and atomic oxygen is also possible [McNesby et al, 1962 ; Stief, 1966]

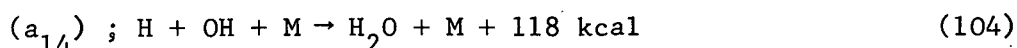


The exact process is not yet known [Cottin et al, 1966 ; Welge and Stuhl, 1967] since the probability of process (102) is a small fraction of the general process



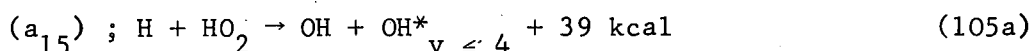
which leads to H atoms with high kinetic energy. Thus, it seems that, from an aeronomic point of view, process (103) is the principal mechanism for H_2O dissociation in the upper mesosphere and lower thermosphere while (101) represents between 1 and 10 % of the total. As far as the photodissociation (102) leading to H_2 is concerned, it is not certain whether it is a sufficiently large fraction to be considered in the upper mesosphere [Cottin et al, 1966]. In any case, such a process can be neglected in the aeronomic analysis of the H_2O photolysis, but perhaps not in the production of molecular hydrogen at mesospheric levels.

When photodissociation of water vapor proceeds through (103) its re-formation may occur through



which is not important compared to other possible aeronomic processes.

The reaction of hydrogen atoms and perhydroxyl radicals leads to two hydroxyl radicals

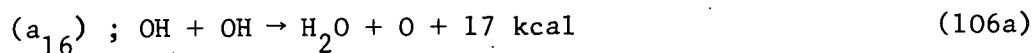


a reaction which has been observed [Cashion and Polanyi, 1959]. With

$$a_{15} = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (105b)$$

the experimental conditions can be followed [Kaufman, 1964].

The reaction between two hydroxyl radicals lead to the re-formation of water vapor

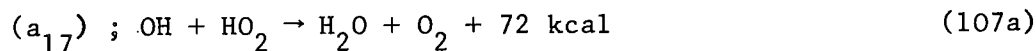


with an activation energy not greater than 2 kcal. All the measurements have been made at 300°K and the correct value is not yet known with sufficient precision. [Dixon-Lewis et al, 1966; Kaufman, 1969; Breen and Glass, 1970]. Thus, the following rate coefficient, which is adopted for stratospheric and mesospheric conditions

$$a_{16} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (106b)$$

leads to about $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ near the mesopause (170°K) and $2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ near the stratopause (270°K).

In the same way, the reaction between hydroxyl and perhydroxyl radicals leads to H_2O .



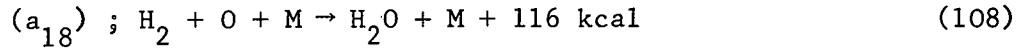
with a small activation energy (~ 1 kcal). There is no direct measurement [Kaufman, 1969], but

$$a_{17} = 3 \times 10^{-12} T^{1/2} e^{-500/T} \text{ cm}^3 \text{ sec}^{-1} \quad (107b)$$

which is adopted for aeronomic applications leads to $1.7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at the mesopause and $8 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at the stratopause.

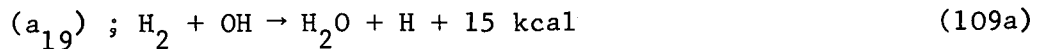
Other reactions can lead to the formation of H_2O , but they are not important in the mesosphere and stratosphere compared with other reactions

leading to its re-formation. The three-body association



should have a small rate coefficient since it is spin forbidden when normal oxygen atoms are involved. Such a reaction is, therefore, neglected.

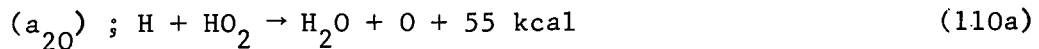
The exothermic reaction between H_2 and OH



requires a relatively high activation energy. With a steric hindrance factor of about 0.01 the measurements at 300 - 500°K [Greiner, 1969] lead to

$$a_{19} = 2.0 \times 10^{-13} T^{1/2} e^{-1800/T} \text{ cm}^3 \text{ sec}^{-1} \quad (109b)$$

Finally, in addition to (105), the reaction between hydrogen atoms and perhydroxyl radicals may lead to the re-formation of H_2O .



with a rate coefficient less important than a_{15} . We adopt the following working value

$$a_{20} = 1.5 \times 10^{-12} T^{1/2} e^{-2000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (110b)$$

If only (105) to (110) are involved in the production of H_2O , equilibrium conditions are

$$n(\text{H}_2\text{O}) \left\{ J_{\text{H}_2\text{O}} + a_{18}^* n[\text{O}(^1\text{D})] \right\} = a_{20} n(\text{HO}_2) n(\text{H}) + \\ [a_{16} n(\text{OH}) + a_{17} n(\text{HO}_2)] n(\text{OH}) + a_{19} n(\text{OH}) n(\text{H}_2) \quad (111A)$$

An approximation for mesospheric conditions can be

$$n(\text{H}_2\text{O}) \left\{ J_{\text{H}_2\text{O}} + a^*_{\text{H}_2\text{O}} n[\text{O}(^1\text{D})] \right\} \simeq a_{17} n(\text{HO}_2) n(\text{OH}) \quad (111\text{B})$$

Since the ratio of $n(\text{HO}_2)/n(\text{OH})$ (see Table IV) is about 0.8 in the mesosphere, it is possible to obtain an idea of the possible concentration of the hydroxyl and perhydroxyl radicals if the water vapor concentration is known. With the mixing ratio 6.5×10^{-6} , numerical values of $n(\text{HO}_2) n(\text{OH})$ can be obtained; they are not less than 10^{15} cm^{-6} and lead to OH and HO_2 concentrations greater than 10^7 cm^{-3} . However, in the upper mesosphere (111b) does not represent the real conditions since hydrogen is involved in the chemical equilibrium of hydroxyl and hydroxyl radicals (equations 41). In any case at the stratopause the concentrations which are $n(\text{OH}) \simeq n(\text{HO}_2) = 5 \times 10^7 \text{ cm}^{-3}$, correspond to a total dissociation rate of $10^4 \text{ H}_2\text{O} \text{ molecules cm}^{-3} \text{ sec}^{-1}$, and are practically photochemical equilibrium values.

Thus there is a clear indication that in the whole stratosphere the dissociation of water vapor does not modify its vertical distribution if the reaction between OH and HO_2 giving H_2O , plays a leading role. Furthermore, the diffuse upward current due to eddy diffusion, which is needed in order to maintain CH_4 at the stratopause, is not needed by H_2O . Considering the destruction of H_2O in the stratosphere principally by its reaction with $\text{O}(^1\text{D})$ atoms (cf Fig. 12) it is possible to consider the eddy diffusion coefficients which would be needed (cf CH_4) with no re-formation of water vapor. Fig. 14 shows the increasing ratios of the eddy diffusion coefficients which would be necessary in the stratosphere. Since there is a continuous re-formation of H_2O , no transport is needed to maintain its normal distribution with altitude. However, in the mesosphere, where the OH and HO_2 concentrations decrease, the re-formation of water vapor is too slow and a diffuse upward current of H_2O is required. Fig. 15 shows that the mesospheric photodissociation requires an eddy diffusion coefficient

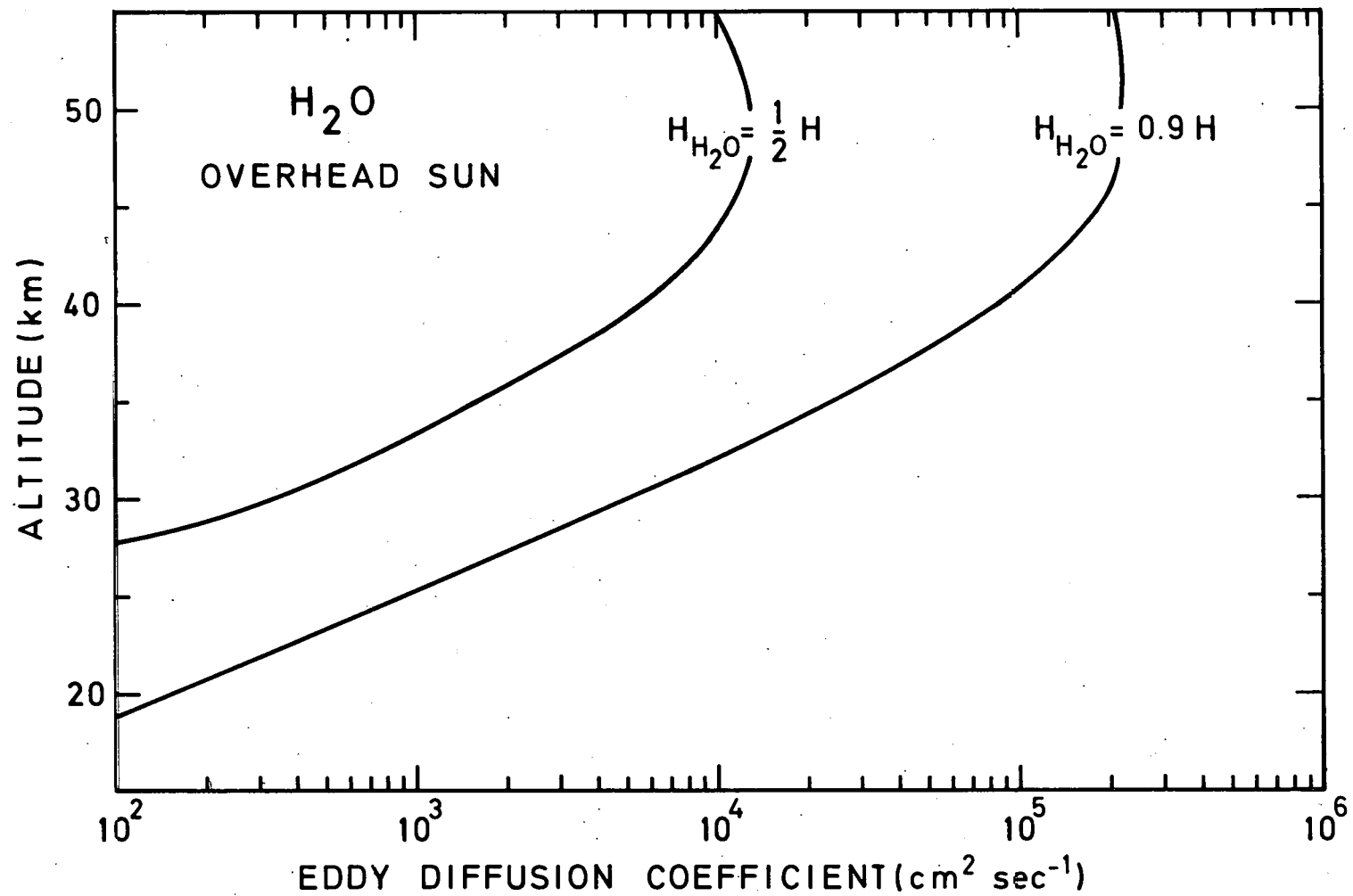


Fig. 14.- Eddy diffusion coefficients which would be necessary in the stratosphere to maintain H_2O assuming that there is no re-formation. See Fig. 11.

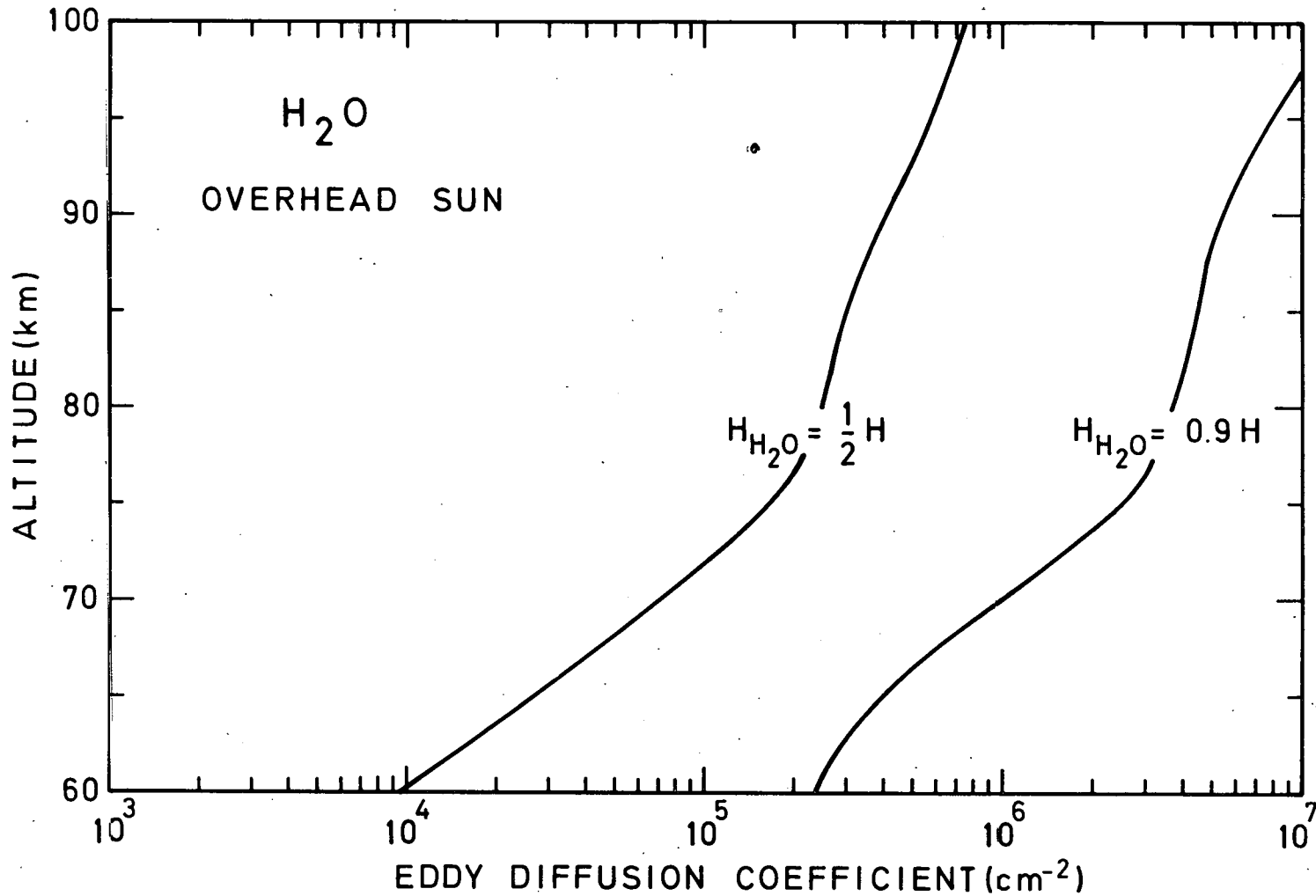


Fig. 15.- Eddy diffusion coefficients which are required in the mesosphere and lower thermosphere to maintain H₂O which is subject to photodissociation.

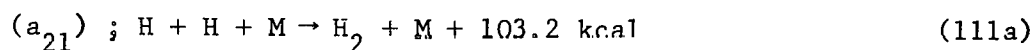
greater than $10^6 \text{ cm}^2 \text{ sec}^{-1}$ to maintain a mixing distribution at the mesopause. The eddy diffusion coefficient increases up to $10^7 \text{ cm}^2 \text{ sec}^{-1}$ at 100 km if mixing of water vapor is adopted at 100 km.

Thus, the aeronomic problem of water vapor in the mesosphere depends on the photochemical conditions that are adopted at the stratopause and on the vertical distribution of the eddy diffusion coefficient above the stratopause.

A coefficient less than $2 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$ (see Fig. 15) would lead to a significant reduction of the mixing ratio since $H_{\text{H}_2\text{O}} \leq \frac{1}{2} H_M$, the H_2O scale height being less than half of the atmospheric scale height. Values reaching $4 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$ are necessary to maintain an almost constant mixing ratio up to the mesopause. It is clear that the vertical distribution of H_2O in the neighbourhood of the mesopause and in the lower mesosphere, and also the aeronomic conditions for other minor constituents, will depend on the choice made for the eddy diffusion coefficient in the calculations of the diffuse upward current. Special care should be taken to avoid unrealistic values for the diffusion coefficients.

VII. MOLECULAR HYDROGEN

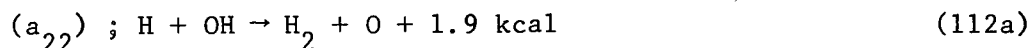
Molecular hydrogen, which is a permanent constituent of the troposphere, may be produced at high altitude by the three-body association of two hydrogen atoms



with the conventional value [Larkin and Thrush, 1964 ; Bennett and Blackmore, 1968] for mesospheric conditions

$$a_{21} = 1 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1} \quad (111b)$$

The bimolecular reaction



requires a high activation energy (see its reverse reaction 114). Its rate coefficient must be between

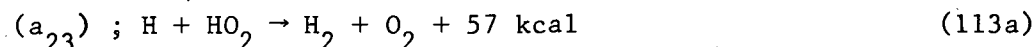
$$a_{22} = 5 \times 10^{-13} T^{1/2} e^{-4400/T} \text{ cm}^3 \text{ sec}^{-1} \quad (112b)$$

with the largest activation energy, and

$$a_{22} = 2 \times 10^{-13} T^{1/2} e^{-3400/T} \text{ cm}^3 \text{ sec}^{-1} \quad (112c)$$

with the lowest activation energy.

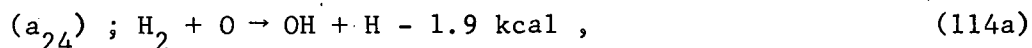
In fact a more important mode of molecular hydrogen formation occurs through the reaction of hydrogen atoms with perhydroxyl radicals



which has a coefficient of about $3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K [Kaufman 1964, 1969]. Thus, it is possible to assume an activation energy not greater than 2 kcal in order to write

$$a_{23} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (113b)$$

The reaction



which is endothermic by about 1.9 kcal, cannot be neglected as a loss process in the thermosphere where the temperature is relatively high.

From the experimental observations [Clyne and Thrush, 1963 ; Wong and Potter, 1965 ; Ripley and Gardiner, 1966 ; Westenberg and De Haas, 1967 ; Campbell and Thrush, 1968]

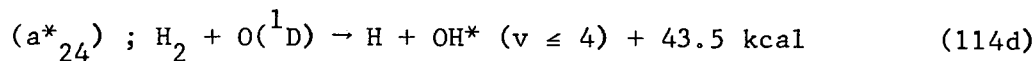
$$a_{24} = 2.5 \times 10^{-12} T^{1/2} e^{-5000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (114b)$$

with the highest activation energy or

$$a_{24} = 5 \times 10^{-13} T^{1/2} e^{-4400/T} \text{ cm}^3 \text{ sec}^{-1} \quad (114c)$$

with the lowest activation energy. It is difficult to make a choice between the various values.

The photodissociation of H_2 [Dalgarno and Allison, 1969 ; Mentall and Gentieu, 1970] can be ignored in the mesosphere. The threshold for a possible dissociation by ultraviolet absorption which lies at 1109 Å [Stecher and Williams] and that for direct photodissociation at 845 Å are in a spectral region where radiation is absorbed in the thermosphere. The photodissociation coefficient will be taken for the calculation in the mesosphere as $a_{25} = 0$. In fact the most important process is the reaction of molecular hydrogen with excited oxygen atoms



for which we adopt the following round figure

$$a_{24}^* = 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$$

since it is not yet possible to deduce an exact value for the various quenching rate coefficients of $\text{O}(^1\text{D})$ deduced from laboratory measurements. Values $a_{24}^* = (1.5 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ are possible.

Thus the chemical conditions for molecular hydrogen are written as follows

$$\frac{dn(H_2)}{dt} + n(H_2) \left[\left\{ a_{18} n(M) + a_{24} \right\} n(O) + a_{19} n(OH) + a_{24}^* n^*(O) \right]$$

$$n(H_2O) J_{H_2-O} + n(H) \left[a_{21} n(M) n(H) + a_{22} n(OH) + a_{23} n(HO_2) \right]$$

(115a)

Considering the numerical values of the various rate coefficients (115) can be written, with a sufficient by good approximation,

$$\frac{dn(H_2)}{dt} + n(H_2) \left[a_{24} n(O) + a_{24}^* n^*(O) \right] = n(H) n(HO_2) a_{23} \quad (115b)$$

In the stratosphere, the reaction between $O(^1D)$ and H_2 plays a role whereas that between $O(^3P)$ and H_2 is not negligible in the thermosphere where the temperature is relatively high. The H_2 production is particularly important in the upper mesosphere where the product $n(H) n(HO_2)$ is maximum.

If the hypothesis of a constant mixing of H_2 in the stratosphere is adopted, it requires high eddy diffusion coefficients (identical to CH_4 , see Fig. 11) which cannot be accepted. Alternatively it must be assumed that the total dissociation, which is 2.6×10^9 H_2 molecules $cm^{-2} sec^{-1}$ for overhead sun conditions, is replaced by an identical downward transport of H_2 molecules formed in the upper mesosphere.

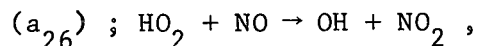
Thus more molecular hydrogen is produced below the mesopause than is destroyed there ; molecular hydrogen from this layer flows downwards into the upper stratosphere where process (114d) converts it into atomic hydrogen and hydroxyl radicals. Such a process which occurs

only in a sunlit atmosphere should lead to not less than 10^9 dissociations $\text{cm}^{-2} \text{sec}^{-1}$ if the mixing ratio $n(\text{H}_2)/n(\text{M}) = 5 \times 10^{-7}$ is maintained. The exact distribution depends on the eddy diffusion coefficient which is introduced into the continuity equation

$$\frac{\partial n(\text{H}_2)}{\partial t} + \frac{\partial [n(\text{H}_2)w]}{\partial z} + a_{24}^* n^*(\text{O}) + a_{24} n(\text{O}) = a_{23} n(\text{H}) n(\text{OH}) \quad (116)$$

where w is the diffusion velocity. A reliable estimate of the concentration of molecular hydrogen cannot be made without an exact knowledge of the values of the eddy diffusion coefficient. In any case, it seems that the stratospheric concentration of molecular hydrogen depends on its production in the upper mesosphere and on its downward transport.

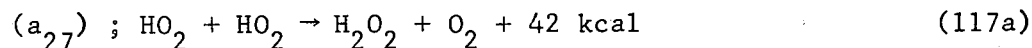
Various reactions with nitrogen oxides in which H, OH, and HO_2 are involved will be introduced in another section. However, a reaction such as



for which the rate coefficient is not known, cannot be forgotten in the stratosphere where the reaction with atomic oxygen is not important enough.

VIII. HYDROGEN PEROXIDE

In the foregoing discussion hydrogen peroxide was considered to be of minor importance and its reactions were not listed. However, it is produced by a two-body process



with a rate coefficient which does not require a high activation energy [Foner and Hudson, 1962]. With $a_{27} = 3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K , the following value which is similar to a_{16} can be adopted

$$a_{27} = 5 \times 10^{-12} T^{1/2} e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (117b)$$

The photodissociation of H_2O_2 is known from laboratory measurements [Urey et al, 1929 ; Holt et al, 1948]. The photodissociation coefficient for zero optical depth is

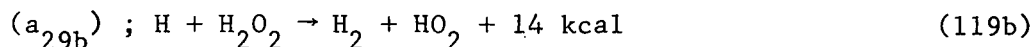
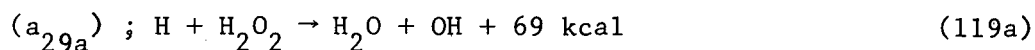
$$J_{\text{H}_2\text{O}_2} = 1.2 \times 10^{-4} \text{ sec}^{-1} \quad (118a)$$

The essential process in the stratosphere is



since the photolysis cannot occur in the far ultraviolet and below 2100 Å the photodissociation coefficient is less than 10^{-5} sec^{-1} . The variation of $J_{\text{H}_2\text{O}_2}$ with the solar zenith angle is shown in Fig. 16. In the lower stratosphere the photodissociation coefficient is less than 10^{-5} sec^{-1} .

The reaction with atomic hydrogen leads to



Experimental evidence [Foner and Hudson 1962b ; Baldwin et al, 1964 ; Hata and Giguère, 1966] seems to indicate that the activation energies of (119a) and (119b) are relatively high, and that $a_{29a} > a_{29b}$. We write

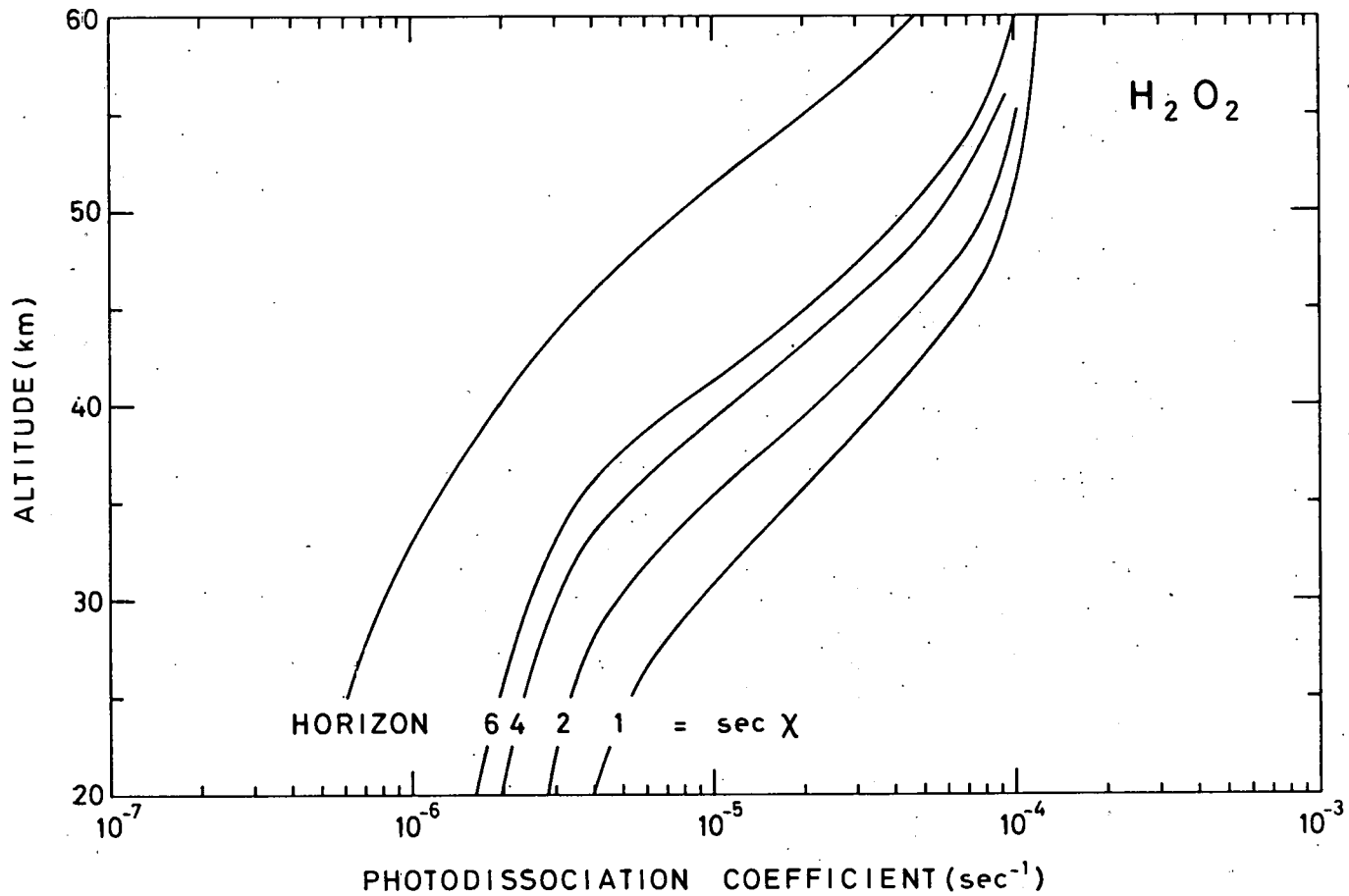
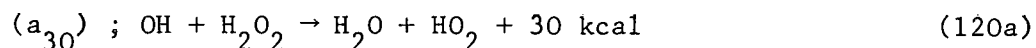


Fig. 16.- Photodissociation coefficient of hydrogen peroxide in the stratosphere for various solar zenith angles. From overhead sun conditions, $\chi = 0$, to $\chi = 90^\circ$, horizon.

$$a_{29a} = 5 \times 10^{-12} T^{1/2} e^{-3000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (119c)$$

$$a_{29b} = 5 \times 10^{-12} T^{1/2} e^{-4500/T} \text{ cm}^3 \text{ sec}^{-1} \quad (119d)$$

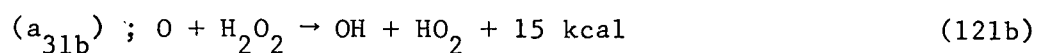
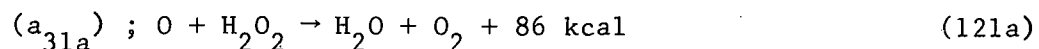
which show that the reaction between H and H_2O_2 is not rapid in aeronomic conditions. But the reaction between a hydroxyl radical and hydrogen peroxide



is more important since its activation energy is of the order of 1 kcal [Greiner, 1968]. Its rate coefficient is about

$$a_{30} = 3 \times 10^{-13} T^{1/2} e^{-500/T} \text{ cm}^3 \text{ sec}^{-1} . \quad (120b)$$

Finally, the reaction between oxygen atoms and hydrogen peroxide molecules must be introduced since atomic oxygen is an important minor constituent

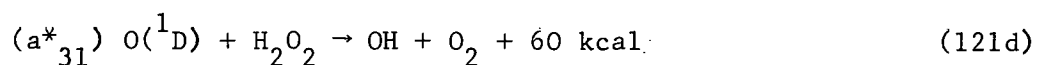


It appears [Foner and Hudson, 1962b] that $a_{31a} > a_{31b}$. With an activation energy of the order of 4 kcal ,

$$a_{31a} = 1.5 \times 10^{-13} T^{1/2} e^{-2000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (121c)$$

leads to a rate coefficient of about $3 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ at 293°K.

Experimental evidence does not rule out $\text{O}(\text{}^1\text{D}) - \text{H}_2\text{O}_2$ reactions such as

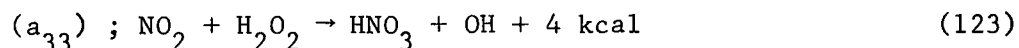
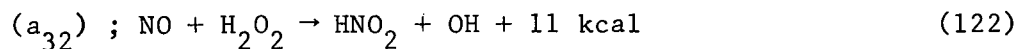


which could have no activation energy and could occur at rate similar to the reactions of O^* with O_3 , H_2 , H_2O or CH_4 . However, the photodissociation coefficient $J_{H_2O_2}$ is greater than $a^* n^*(O)$ and remains the most important loss process of H_2O_2 .

If nitric oxide is involved, hydrogen peroxide decomposes according to overall reactions such as



which may come, for example, from



for which the rate coefficients are not known. NO_2 and NO concentrations of the order of 10^9 cm^{-3} in the stratosphere would lead to a rate coefficient less than 10^{-5} sec^{-1} if $a_{32} \geq 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$.

If all reactions from (117) to (122) are considered in the production and destruction of H_2O_2 the differential equation for H_2O_2 is

$$\frac{dn(H_2O_2)}{dt} + n(H_2O_2) \left[J_{H_2O_2} + \left\{ a_{29a} + a_{29b} \right\} n(H) + a_{30} n(OH) + \left\{ a_{31a} + a_{31b} \right\} n(O) + a_{32} n(NO) + a_{33} n(NO_2) \right] = a_{27} n^2(HO_2) \quad (124a)$$

Since for overhead sun conditions $J_{\text{H}_2\text{O}_2}$ is about 10^{-4} sec^{-1} and $4 \times 10^{-6} \text{ sec}^{-1}$ at the stratopause and near 20 km respectively, it is the principal loss term of hydrogen peroxide compared with its reactions with H and OH ; the reaction with atomic oxygen, which reaches a maximum of about 10^{-5} sec^{-1} near the stratopause, is practically negligible compared with the photodissociation. As far as the reactions with nitrogen oxides are concerned, it is not possible to neglect them in the lower stratosphere if their rate coefficients are not less than $10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. Therefore, an idea of the behavior of hydrogen peroxide can be obtained only with the over simplified equation

$$\frac{dn(\text{H}_2\text{O}_2)}{dt} + n(\text{H}_2\text{O}_2) J_{\text{H}_2\text{O}_2} = a_{27} n^2(\text{HO}_2) \quad (124b)$$

Photoequilibrium conditions at the stratopause lead to

$$\frac{n^2(\text{HO}_2)}{n(\text{H}_2\text{O}_2)} = \frac{10^{-4}}{2 \times 10^{-12}} = 5 \times 10^7 \text{ cm}^{-3} \quad (125a)$$

and at 20 km

$$\frac{n^2(\text{HO}_2)}{n(\text{H}_2\text{O}_2)} = \frac{4 \times 10^{-6}}{8 \times 10^{-13}} = 5 \times 10^6 \text{ cm}^{-3} \quad (125b)$$

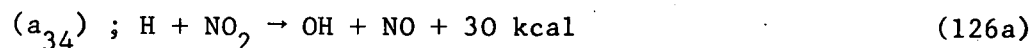
They give a clear indication that the hydrogen peroxide concentration is greater than that of the hydroperoxyl radical at 20 km and is of the same order of magnitude at the stratopause.

Since all the reactions, in which H_2O_2 is involved, except (123), are reactions occurring in a sunlit atmosphere, it is important to know the possible action of nitrogen dioxide. In any case, special experimental data are necessary before the role of hydrogen peroxide in the stratosphere can be determined.

IX. NITROGEN OXIDES

In the foregoing discussion on the reactions in which hydrogen peroxide is involved, a possible action of nitrogen oxide has been indicated. However, other aeronomic reactions with nitrogen oxides can play a role in the stratosphere and mesosphere [Nicolet 1965, 1970].

A rapid reaction [Phillips and Schiff, 1962]

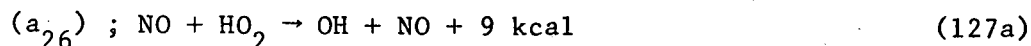


with a rate coefficient

$$a_{34} = 2 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (126b)$$

is not important since the reaction $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ is also rapid and since $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ plays also leading role.

In the mesosphere, the effect of NO on HO_2 and H_2O_2 is also without great importance since $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$ and similar reactions are more important. However, in the stratosphere their action may become important. The reaction



is fast relative to other reactions of HO_2 in similar circumstances [Tyler, 1962]. No data are available on the rate coefficient but assuming two extreme values, with activation energy reaching 2.5 kcal,

$$a_{26a} = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (127b)$$

in order to reach not less than $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 273°K, and

$$a_{26b} = 3 \times 10^{-12} T^{1/2} e^{-1250/T} \text{ cm}^3 \text{ sec}^{-1} \quad (127c)$$

leading to not less than $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 500°K, it is possible to see that a leading role can be played by (127a) in the lower stratosphere. The ratio $n(\text{HO}_2)/n(\text{OH})$ given by (41c) must be modified when (127) is introduced ; it becomes

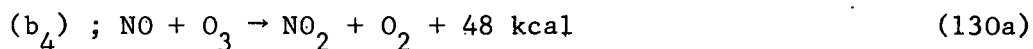
$$\frac{n(\text{HO}_2)}{n(\text{OH})} = \left\{ \frac{a_1 n(\text{M}) n(\text{O}_2) a_5 n(\text{O})}{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)} + a_6 n(\text{O}_3) \right\} \left\{ a_7 n(\text{O}) + a_{26} n(\text{NO}) \right\} \quad (128)$$

Since $n(\text{O})$ decreases rapidly from about 10^9 cm^{-3} at 40 km to $4 \times 10^7 \text{ cm}^{-3}$ at 30 km and to 10^6 cm^{-3} at 20 km, when its value is obtained by (26), it is clear that NO concentrations of the order of 10^9 cm^{-3} can play a role in the stratosphere if the rate coefficient a_{26a} is used. With the lowest value a_{26c} , NO can still play a role at 20 km if its concentration reaches $10^9 \text{ cm}^{-3} \text{ sec}^{-1}$. Consequently, the ratio $n(\text{HO}_2)/n(\text{OH})$ is not yet defined with sufficient precision in the lower stratosphere. It depends on the exact value of the rate coefficient a_6 , which has not been measured, and on the nitric oxide concentration.

If nitric oxide is present in the lower stratosphere, it is clear that nitrogen dioxide must be considered. The ratio [Nicolet, 1965] which corresponds to photochemical equilibrium conditions is

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = 1 \text{ to } 4 \quad (129)$$

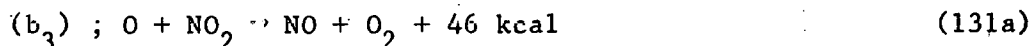
between 20 and 40 km. In addition to the loss process involving O_3 ,



which has been observed in the laboratory [Johnson and Crossby, 1954 ; Phillips and Schiff, 1962a ; Clough and Thrush, 1967] with a rate coefficient which may correspond to

$$b_4 = 5 \times 10^{-14} T^{1/2} e^{-1200/T} \text{ cm}^3 \text{ sec}^{-1}, \quad (130b)$$

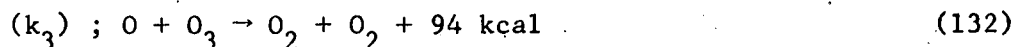
it is necessary to consider the following reaction



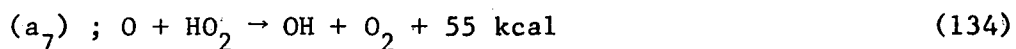
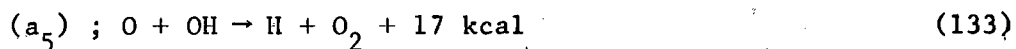
which is relatively rapid [Schiff, 1964 ; Klein and Herron, 1964] with a rate coefficient

$$b_3 = 1.5 \times 10^{-12} T^{1/2} e^{-500/T} \quad (131b)$$

This reaction must be compared with the reaction of atomic oxygen (cf formula 7) with O_3



and with OH and HO_2 (reactions 35 and 37)



Instead of (64) the correction term A becomes

$$A = \left[b_4 \frac{k_2 n(M) n(O_2)}{J_3} n(NO) + b_3 n(NO_2) + a_7 \{n(OH) + n(HO_2)\} \right] / 2k_3 n(O_3) \quad (135)$$

Since $2k_3 n(O_3) > 10^{-3} \text{ sec}^{-1}$ in the major part of the stratosphere, the correction term A plays a role when the various terms in which hydroxyl and hydroperoxyl radicals and nitrogen oxides are involved are greater or of the same order of magnitude. With the mixing ratio which has been used here for H_2O , an effect due to OH and HO_2 occurs in the upper stratosphere since $a_7 n(HO_2) > 10^{-3} \text{ sec}^{-1}$. As far as nitrogen dioxide is concerned an effect requires NO_2 concentrations greater than 10^9 cm^{-3} since its rate coefficient b_3 is of the order of $(3 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$. The effect of nitric oxide is particularly important in the lower stratosphere since its rate coefficient is increased by the ratio $k_2 n(M) n(O_2)/J_3$ which leads to high values of

$$b_{4 \text{ eff}} = b_4 \frac{k_2 n(M) n(O_2)}{J_3} \quad (136)$$

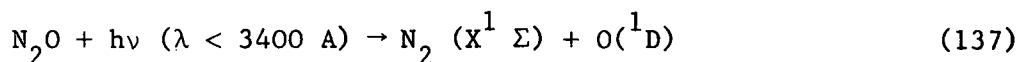
The following values ($\text{cm}^3 \text{ sec}^{-1}$)

	15 km	20	25	30	40	50
b_4	2.5×10^{-15}	3.1×10^{-15}	3.8×10^{-15}	4.7×10^{-15}	9.3×10^{-15}	1.0×10^{-14}
$b_{4 \text{ eff}}$	1.7×10^{-7}	3.1×10^{-8}	4.8×10^{-9}	7.0×10^{-10}	9.6×10^{-12}	1.7×10^{-13}

show that the action of nitric oxide is important when $b_{4 \text{ eff}} n(NO) > 10^{-2} \text{ sec}^{-1}$. Such an effect can easily occur in the stratosphere [Crutzen, 1970].

Finally, the effect of N_2O which has been introduced in the mesosphere [Hesstvedt and Janson, 1969 ; Shimazaki and Lair, 1970] cannot be considered since its formation from N_2 and O in their normal states is not possible. The only possibility of an aeronomic effect due to N_2O is the dissociation of nitrous oxide [Bates and Hays, 1967] in the lower stratosphere.

N_2O is subject to various photodissociation processes in the stratosphere. The principal aeronomic process is



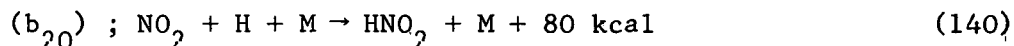
The photodissociation coefficient increases from about $1.5 \times 10^{-9} \text{ sec}^{-1}$, at the beginning of the stratosphere, up to about 10^{-6} sec^{-1} at the stratopause. With such a coefficient and no rapid re-formation of N_2O , its concentration decreases rapidly in the stratosphere. N_2O is practically absent in the mesosphere and does not belong to the system of nitrogen oxides in which NO and NO_2 are involved. However, in the lower stratosphere, the reaction



which has been studied by Greenberg and Heicklen [1970] leads to $k_{38}/k_{39} = 1$. Thus, reaction (139) leads to a formation of nitric oxide in the lower stratosphere where N_2O is present. The total production depends on the eddy diffusion in the stratosphere which is necessary to sustain N_2O subject to photodissociation.

In any case, the problem of nitrogen oxides in the lower stratosphere must be considered in association with nitrogen dioxide and nitrous and nitric acids [Nicolet, 1965]. Nitrous acid is formed in the stratosphere by association of NO with OH and H_2O_2 (Fig. 17) while nitric acid (Fig. 18) seems to be subject to an important production not only from association of NO and NO_2 with HO_2 and OH respectively, but also by a reaction between H_2O_2 and NO_2 .

Three-body associations leading to nitrous and nitric acids must be considered. They are



NITROUS ACID

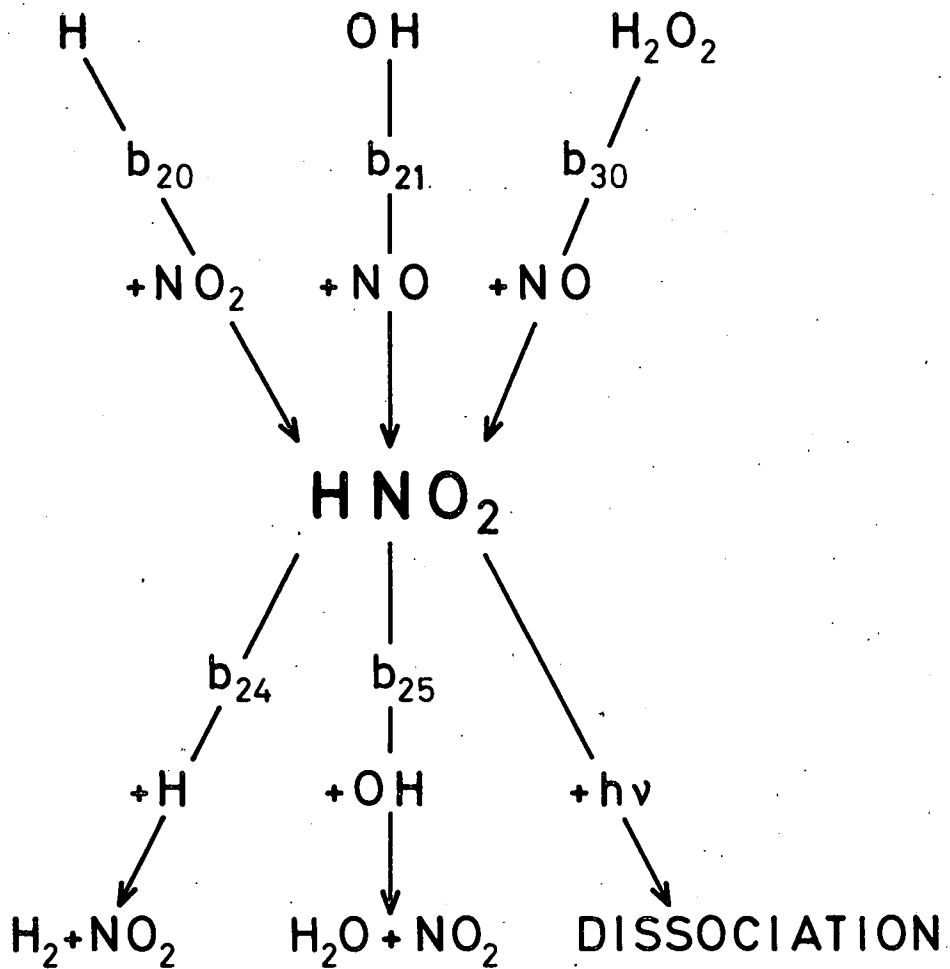


Fig. 17.- Principal reactions in which nitrous acid may be involved in the mesosphere and stratosphere.

NITRIC ACID

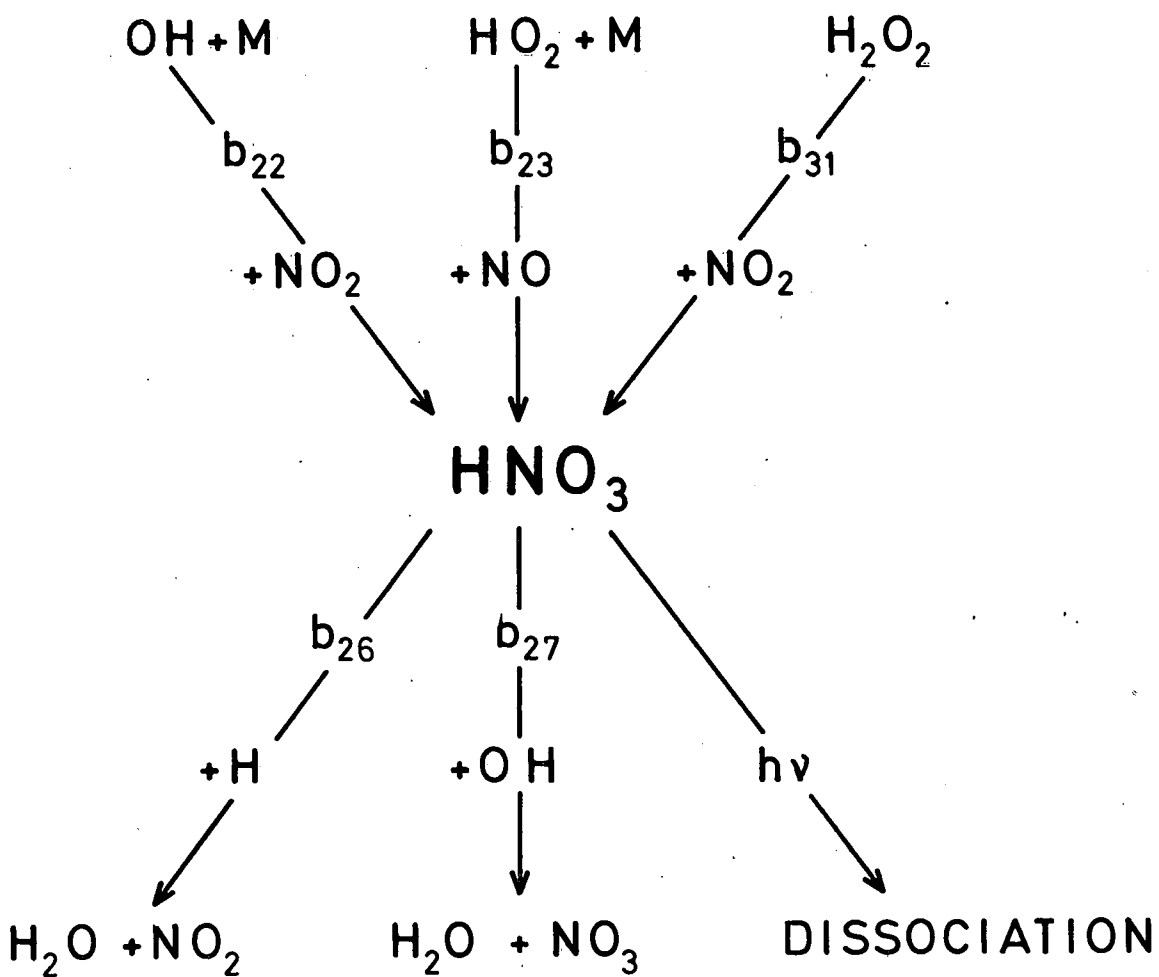
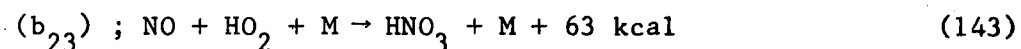
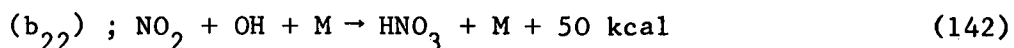
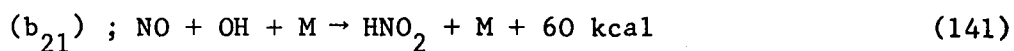
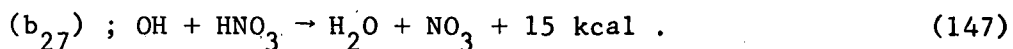
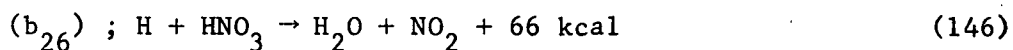
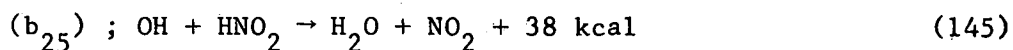
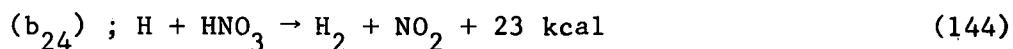


Fig. 18.- Principal reactions in which nitric acid may be involved in the mesosphere and stratosphere.

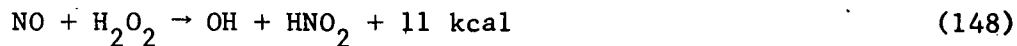


The rate coefficients for (54.70-73) are not known, but typical values for such three-body rate coefficients are between 10^{-32} and $10^{-31} \text{ cm}^6 \text{ sec}^{-1}$. Reaction (140) leading to nitrous acid is not important since it requires H and NO_2 , but it is clear that reactions (141), (142) and (143) may be important in the stratosphere.

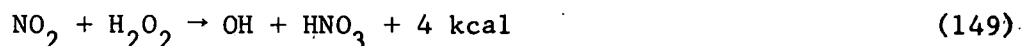
The photodissociation must be included with the loss processes



The reactions (122) and (123) which have been considered before cannot be neglected in the aeronomic discussion. Thus



and



must be added as production processes of nitrous and nitric acids.

All these reactions are exothermic, but their activation energies are not known. Since the reaction of HNO_3 with OH is perhaps the principal loss process, it seems possible that the fraction of nitric acid which is not destroyed after its formation in the stratosphere leads to the disappearance of NO. Thus, it is extremely important to measure the concentration of nitrogen dioxide [Ackerman and Frimout, 1969 ; 1970] or nitric oxide [Pontano and Hale, 1970] simultaneously with that of nitric acid [Murcray et al, 1969 ; Rhine et al, 1969] in order to know the proportions of different nitrogen oxides which are definitively converted into more complex compounds going from the stratosphere into the troposphere. The nitrate plus nitrite content of South Polar snow [Wilson and House, 1965] corresponds to an infall of nitrogen oxide of the order of 1.5×10^7 molecules $\text{cm}^{-2} \text{sec}^{-1}$. In any case, a special study of the photodecomposition of nitrogen trioxide and of nitric acids should be made since their decomposition is of special interest in the aeronomic processes of the stratosphere.

X. GENERAL CONCLUSIONS

When all reactions dealing with H, OH and HO_2 are considered the following general equations can be written

$$\begin{aligned}
 & \frac{dn(\text{H}_2\text{O})}{dt} + n(\text{H}_2\text{O}) \left[J_{\text{OH-H}} + J_{\text{H}_2-\text{O}} + a_{\text{H}_2\text{O}}^* n(\text{O}^*) \right] = \\
 & n(\text{H}) \left[a_{17} n(\text{M}) n(\text{OH}) + a_{20} n(\text{HO}_2) + a_{29a} n(\text{H}_2\text{O}_2) \right] \\
 & + n(\text{OH}) \left[a_{16} n(\text{OH}) + a_{17} n(\text{HO}_2) + a_{19} n(\text{H}_2) + a_{30} n(\text{H}_2\text{O}_2) \right] \\
 & + n(\text{O}) \left[a_{18} n(\text{M}) n(\text{H}_2) + a_{31} n(\text{H}_2\text{O}_2) \right] \quad (150)
 \end{aligned}$$

$$\begin{aligned}
& \frac{dn(\text{H}_2)}{dt} + n(\text{H}_2) \left[\left\{ a_{18} n(\text{M}) + a_{24} \right\} n(\text{O}) + a_{19} n(\text{OH}) + a_{24}^* n(\text{O}) \right] = \\
& n(\text{H}) \left[a_{21} n(\text{M}) n(\text{H}) + a_{22} n(\text{OH}) + a_{23} n(\text{HO}_2) + a_{29b} n(\text{H}_2\text{O}_2) \right] \\
& + n(\text{H}_2\text{O}) J_{\text{H}_2-\text{O}} \tag{151}
\end{aligned}$$

$$\begin{aligned}
& \frac{dn(\text{H}_2\text{O}_2)}{dt} + n(\text{H}_2\text{O}_2) \left[J_{\text{H}_2\text{O}_2} + \left\{ a_{29a} + a_{29b} \right\} n(\text{H}) + a_{30} n(\text{OH}) \right. \\
& \left. + \left\{ a_{31a} + a_{31b} \right\} n(\text{O}) + a_{32} n(\text{NO}) + a_{33} n(\text{NO}_2) + a_{37} n(\text{CO}) \right] = \\
& a_{27} n^2(\text{HO}_2) \tag{152}
\end{aligned}$$

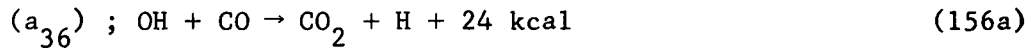
$$\begin{aligned}
& \frac{dn(\text{H})}{dt} + n(\text{H}) \left[a_0 n(\text{M}) n(\text{O}) + a_1 n(\text{M}) n(\text{O}_2) + \left\{ a_2 + a_3 \right\} n(\text{O}_3) + \right. \\
& \left. \left\{ a_{14} n(\text{M}) + a_{22} \right\} n(\text{OH}) + \left\{ a_{15} + a_{20} + a_{23} \right\} n(\text{HO}_2) + 2 a_{21} n(\text{M}) n(\text{H}) \right. \\
& \left. + \left\{ a_{29a} + a_{29b} \right\} n(\text{H}_2\text{O}_2) \right] = n(\text{H}_2\text{O}) J_{\text{OH-H}} + \left[a_5 n(\text{O}) + a_{19} n(\text{H}_2) \right] \\
& n(\text{OH}) + n(\text{H}_2) \left[a_{24} n(\text{O}) + a_{24}^* n(\text{O}^*) \right] \tag{153}
\end{aligned}$$

$$\begin{aligned}
& \frac{dn(\text{OH})}{dt} + n(\text{OH}) \left[\left\{ a_4 n(\text{M}) + a_5 \right\} n(\text{O}) + a_6 n(\text{O}_3) + \left\{ a_{14} n(\text{M}) + a_{12} \right\} n(\text{H}) \right. \\
& \left. + 2a_{16} n(\text{OH}) + a_{17} n(\text{HO}_2) + a_{19} n(\text{H}_2) + a_{30} n(\text{H}_2\text{O}_2) + a_{36} n(\text{CO}) \right] = \\
& n(\text{H}) \left[a_0 n(\text{M}) n(\text{O}) + a_2 n(\text{O}_3) + a_{15} n(\text{HO}_2) \right] \\
& + n(\text{HO}_2) \left[J_{\text{HO}_2} + a_{6b} n(\text{O}_3) + a_7 n(\text{O}) + a_{15} n(\text{H}) + a_{26} n(\text{NO}) \right] \\
& + n(\text{H}_2\text{O}_2) \left[2 J_{\text{H}_2\text{O}_2} + a_{29a} n(\text{H}) + a_{31b} n(\text{O}) + a_{32} n(\text{NO}) + a_{33} n(\text{NO}_2) \right] \\
& + n(\text{H}_2) \left[a_{24} n(\text{O}) + a_{24}^* n(\text{O}^*) \right] + n(\text{H}_2\text{O}) \left[J_{\text{H-OH}} + 2a_{\text{H}_2\text{O}}^* n(\text{O}^*) \right] \\
& + 4 n(\text{CH}_4) \left[a_{\text{CH}_4} n(\text{O}) + a_{\text{CH}_4}^* n(\text{O}^*) \right]
\end{aligned} \tag{154}$$

$$\begin{aligned}
& \frac{dn(\text{HO}_2)}{dt} + n(\text{HO}_2) \left[J_{\text{HO}_2} + a_{6b} n(\text{O}_3) + a_7 n(\text{O}) + \left\{ a_{15} + a_{20} + a_{23} \right\} \right. \\
& \left. n(\text{H}) + a_{17} n(\text{OH}) + 2a_{27} n(\text{HO}_2) + a_{26} n(\text{NO}) \right] = \\
& \left[a_1 n(\text{M}) n(\text{O}_2) + a_3 n(\text{O}_3) \right] n(\text{H}) + \left[a_4 n(\text{M}) n(\text{O}) + a_6 n(\text{O}_3) \right] n(\text{OH}) \\
& + \left[a_{29b} n(\text{H}) + a_{30} n(\text{OH}) + a_{31b} n(\text{O}) \right] n(\text{H}_2\text{O}_2)
\end{aligned} \tag{155}$$

All the reactions which were discussed in the preceding sections have been introduced in equations (150) to (155) with the addition of two reactions of OH and HO₂ with CO which may play a role in the lower stratosphere.

The reaction

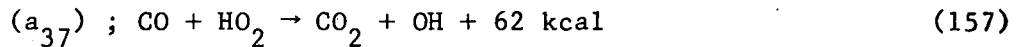


has been observed between 300°K and 500°K [Greiner, 1969] with practically no activation energy. The rate coefficient would be about

$$a_{36} = 10^{-13} \text{ cm}^3 \text{ sec}^{-1} . \quad (156b)$$

An analysis should be made of the reactions between carbon monoxide with hydroperoxyl radicals and hydrogen peroxide in order to determine the exact chemical behavior of the minor constituents in the lower stratosphere.

For example, a study should be made of



for which the rate coefficient a_{37} is not known.

In order to give an idea of the reactions which play a real role in the aeronomic behavior of H₂O and H₂ and the various radicals H, OH, HO₂ and H₂O₂, Fig. 19 shows a general scheme. It is clear that H, OH and HO₂ may be in equilibrium when reactions with atomic oxygen are sufficiently rapid. From (153), (154) and (155), we can write

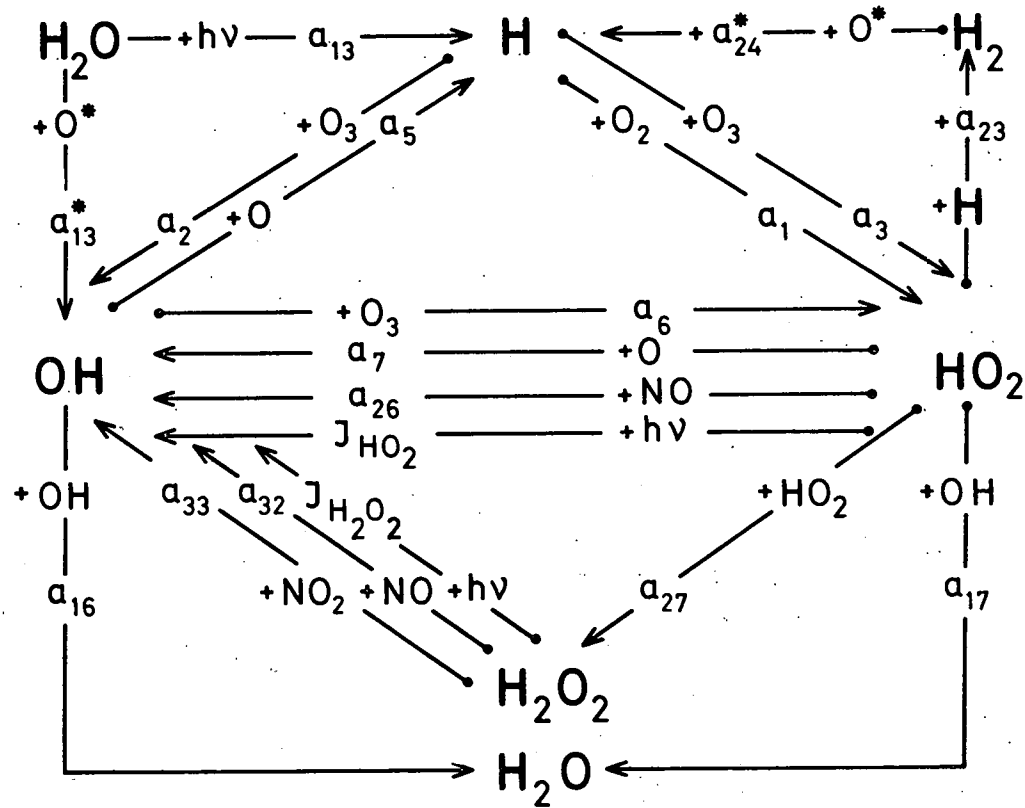


Fig. 19.- Fundamental H₂O reaction scheme. Initiating and terminating reactions depend on the production and destruction of hydroxyl radicals. Nitrogen oxides must be involved in the lower stratosphere.

$$\begin{aligned}
& \frac{dn(H)}{dt} + \frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + \\
& 2 n(H) \left[\left\{ a_{15} n(M) + a_{22} \right\} n(OH) + \left\{ a_{20} + a_{23} \right\} n(HO_2) + a_{21} n(M) n(H) \right] \\
& + 2n^2(OH) a_{16} + 2a_{17} n(OH) n(HO_2) + 2n^2(HO_2) a_{27} = \\
& 2n(H_2O) \left[J_{OH-H} + a_{H_2O}^* n(O^*) \right] + 2n(H_2O_2) \left[J_{H_2O_2} + a_{31b} n(O) \right] \\
& + 2n(H_2) \left[a_{24} n(O) + a_{24}^* n(O^*) \right] + 4n(CH_4) \left[a_{CH_4} n(O) + a_{CH_4}^* n(O^*) \right]
\end{aligned} \tag{158}$$

If $a_7 n(O) + J_{HO_2}$ is greater than 10^{-3} sec^{-1} equilibrium conditions can be considered in (155), and $dn(HO_2)/dt = 0$. Considering the essential reactions (Fig. 19), we can write

$$\begin{aligned}
n(HO_2) \left[J_{HO_2} + a_7 n(O) + a_{26} n(NO) \right] &= a_1 n(M) n(O_2) n(H) + \\
a_6 n(O_3) n(OH) + a_{31b} n(O) n(HO_2) &
\end{aligned} \tag{159a}$$

Since $a_7 n(O) > 10^{-3} \text{ sec}^{-1}$ above 30 km for overhead sun conditions (see Fig. 20), (159a) is certainly correct in the upper stratosphere and in the whole mesosphere and lower thermosphere. At the stratopause and in the mesosphere (159a) can be simplified and is written (cf 41g)

$$\frac{n(HO_2)}{n(H)} = \frac{a_1 n(M) n(O_2)}{a_7 n(O)} \tag{159b}$$

In the same way, when $a_1 n(M) n(O_2) + a_2 n(O_3) > 10^{-3} \text{ sec}^{-1}$, i.e. (Fig. 20) below the mesopause in the whole mesosphere and stratosphere,

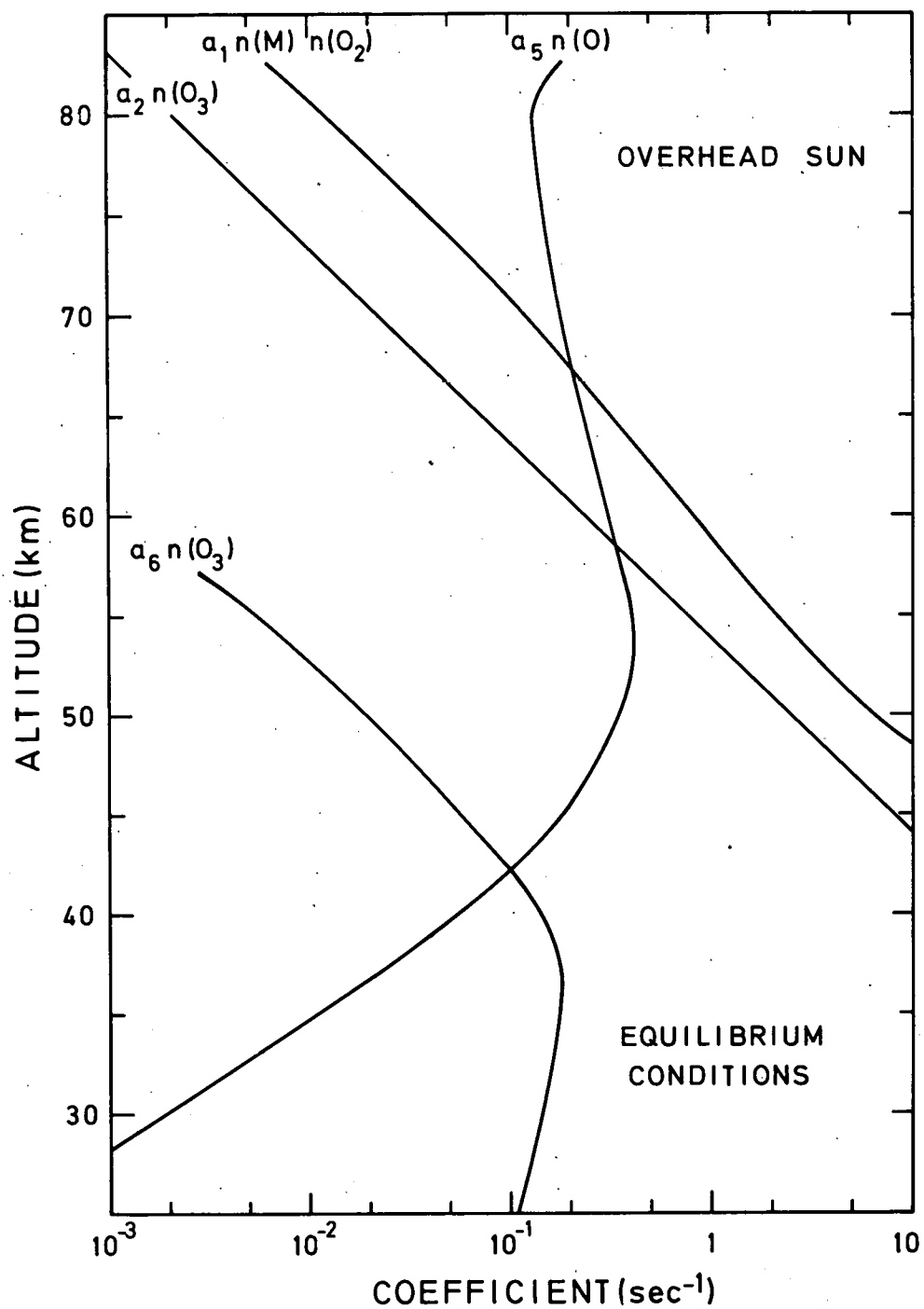


Fig. 20.- Reaction coefficients indicating that the times which are involved are less than 10^{-3} sec⁻¹ above 30 km.

$dn(H)/dt = 0$ and (153) becomes (see Fig. 19) with the essential reactions

$$n(H) \left[a_1 n(M) n(O_2) + a_2 n(O_3) \right] = a_5 n(O) n(OH) +$$

$$n(H_2O) J_{OH-H} + n(H_2) \left[a_{24}^* n(O^*) \right] \quad (160a)$$

In the major part of the stratosphere and the mesosphere (160a) becomes practically

$$\frac{n(OH)}{n(H)} = \frac{a_1 n(M) n(O_2) + a_2 n(O_3)}{a_5 n(O)} \quad (160b)$$

which is (41b).

Thus, at the stratopause equilibrium conditions can be used, and

$$\frac{n(OH)}{n(HO_2)} = \frac{a_1 n(M) n(O_2) + a_2 n(O_3)}{a_1 n(M) n(O_2)} \quad (161)$$

is the equation which must be used in the mesosphere and lower thermosphere.

Equation (158) can be applied to the upper mesosphere or to the lower mesosphere if different conditions are considered. It is clear (see Fig. 20 and Table IV) that the ratios $n(HO_2)/n(H)$ and $n(OH)/n(H)$ increase from values < 1 at the mesopause to values > 1 at the stratopause.

At the mesopause and above (158) becomes

$$\frac{dn(H)}{dt} + 2n(H) \left[a_{23} n(HO_2) \right] = P(H) \quad (162a)$$

where $P(H)$ corresponds to all possible production processes, but principally the photodissociation of water vapor.

With (159b), (162a) is written

$$\frac{dn(H)}{dt} + 2n^2(H) a_{23} \frac{a_1 n(M) n(O_2)}{a_7 n(O)} = P(H) \quad (162b)$$

which shows that several days are required at the mesopause to reach equilibrium conditions. For this reason, mixing conditions lead to the best approximation for the vertical distribution of atomic hydrogen in the lower thermosphere. The introduction of eddy and molecular diffusion in the aeronomic problem of atomic hydrogen requires special attention.

Below 60 km $a_5 n(O) < a_1 n(M) n(O_2) + a_2 n(O_3)$, and it can be said that the stratopause conditions are, from (158),

$$\begin{aligned} \frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + 2n^2(OH) a_{16} + 2a_{17} n(OH) n(HO_2) + 2n^2(HO_2) a_{27} = \\ 2n(H_2O) \left[J_{OH-H} + a_{H_2O}^* n(O^*) \right] + 2n(H_2O_2) \left[J_{H_2O_2} + a_{31b} n(O) \right] \end{aligned} \quad (163)$$

The essential fact is that equilibrium conditions can be applied in the major part of the stratosphere and mesosphere, since an important fraction of the photochemical equilibrium can be reached in less than three hours. Furthermore, there is a variation between day and night [Nicolet, 1964, 1970] which leads to a re-formation of H_2O . It can be concluded that there is no difficulty in maintaining a normal vertical distribution for H_2O . Nevertheless, the role of hydrogen peroxide in the stratosphere should be defined when exact rate coefficients are known. A complete simplification of (152) which would lead to

$$\frac{dn(H_2O_2)}{dt} + n(H_2O_2) J_{H_2O_2} = a_{27} n^2(HO_2) \quad (164)$$

indicates that equilibrium conditions for (163) can be written in the following form

$$a_{16} n^2(\text{OH}) + a_{17} n(\text{OH}) n(\text{HO}_2) = n(\text{H}_2\text{O}) \left[J_{\text{OH-H}} + a_{\text{H}_2\text{O}}^* n(\text{O}^*) \right] \quad (165a)$$

and with (161)

$$n^2(\text{OH}) \left[\frac{a_1 n(\text{M}) n(\text{O}_2)}{a_1 n(\text{M}) n(\text{O}_2) + a_2 n(\text{O}_3)} a_{17} + a_{16} \right] = n(\text{H}_2\text{O}) \left[J_{\text{OH-H}} + a_{\text{H}_2\text{O}}^* n(\text{O}^*) \right] \quad (165b)$$

such an equation leads to the following average concentrations

	40 km	50 km	60 km
n(OH)	$8 \times 10^7 \text{ cm}^{-3}$	$6 \times 10^7 \text{ cm}^{-3}$	$3 \times 10^7 \text{ cm}^{-3}$

which can be accepted as approximate values representing average daytime concentrations.

As far as molecular hydrogen is concerned a special analysis is required. Keeping the essential reactions in (151), the simplified equation is (cf Fig. 19)

$$\frac{dn(\text{H}_2)}{dt} + n(\text{H}_2) \left[a_{24} n(\text{O}) + a_{24}^* n(\text{O}^*) \right] = n(\text{H}) a_{23} n(\text{HO}_2) + n(\text{H}_2\text{O}) J_{\text{H}_2-\text{O}} \quad (166)$$

and it shows that there is an important production process near the mesopause and two important loss processes near the stratopause and in the

thermosphere, respectively. Eddy and molecular diffusion processes must play an important role in the vertical distribution of molecular hydrogen.

Finally, equation (150) shows that in the lower thermosphere the re-formation of H_2O is not important, and that its photodissociation must be associated with eddy and molecular diffusion processes which determine its vertical distribution.

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