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Ozone and Hydrogen Reactions

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FOREWORD

"Ozone and Hydrogen Reactions" was presented at the General Scientific Assembly of the International Association of Geomagnetism and Aeronomy (IAGA), Madrid September 1-13, 1969 as a short invited paper and is a Scientific Report n° 350, March 10, 1970 of the Ionosphere Research Laboratory, Pennsylvania State University. It will be published in Annales de Géophysique, 26,1970.

AVANT-PROPOS

"Ozone and Hydrogen Reactions" est l'exposé développé d'une courte communication donnant les résultats essentiels présentée à Madrid lors de l'Assemblée Scientifique Générale de l'Association Internationale de Géomagnétisme et d'Aéronomie, Septembre 1-13, 1969. Cet exposé, qui est également présenté comme Scientific Report n° 350, March 10, 1970, Ionosphere Research Laboratory, The Pennsylvania State University, paraîtra dans le volume 26,1970 des Annales de Géophysique .

VOORWOORD

"Ozon en waterstofreacties" is voorgedragen geworden op de Algemene Wetenschappelijke Vergadering van de Internationale Vereniging voor Geomagnetisme en Aeronomie, te Madrid van 1 tot 13 september 1969. Deze uiteenzetting is reeds verschenen als het Scientific Report n° 350, March 10, 1970, Ionosphere Research Laboratory, The Pennsylvania State University en zal verder verschijnen in de Annales de Géophysique, band 26, 1970.

VORWORT

"Ozone and Hydrogen Reactions" wurde in Madrid als eine kurze eingeladene Arbeit zur "Assemblée Scientifique Générale de l'Association Internationale de Géomagnétisme et d'Aéronomie", 1-13 September, 1969 vorgestellt. Diese Arbeit ist auch als "Scientific Report nr 350, March 10, 1970, Ionosphere Research Laboratory, The Pennsylvania State University", vorgestellt und wird in "Annales de Géophysique, 26, 1970" herausgegeben werden.

OZONE AND HYDROGEN REACTIONS

by

M. NICOLET

Abstract

Solar radiation dissociates water vapor into hydrogen atoms and hydroxyl radicals in the thermosphere and upper mesosphere. In the stratosphere and lower mesosphere, dissociation of H_2O is brought about mainly by a collision process with excited oxygen atoms produced by photodissociation of ozone. Such a collision process prevents the existence of normal mixing ratios for methane and molecular hydrogen at the stratopause. The rate of oxidizing processes falls off more rapidly with increase of altitude than does that of the vertical transport by eddy diffusion.

Hydrogen molecules in the mesosphere are produced as a result of subsequent chemical reactions between hydroperoxyl radicals and hydrogen atoms. Hydrogen acts as a catalyst for the destruction of oxygen atoms and causes the ozone concentration to diminish pronouncedly in the mesosphere, from a factor of 1.5 at the stratopause to about a factor of 100 at the mesopause. The vertical distribution of water vapor is not affected in the stratosphere and mesosphere by the dissociation process since its re-formation is rapid. In the thermosphere, water vapor diffuses into the photodissociative region by eddy diffusion which carries it up at a sufficient rate to replace the hydrogen being lost.

Various reactions involving nitric oxide and nitrogen peroxide must be introduced in the reactions of the stratosphere. Such molecules play an aeronomic role on the ratio of the hydroxyl and hydroperoxyl radical concentrations. In spite of a continuous production of hydrogen peroxide molecules, their concentration should be small. It is thought that reactions with nitrogen oxides lead to nitric and nitrous acid molecules and are the mechanism responsible for the removal of nitric oxide which is produced in the thermosphere.

Résumé

Si la radiation solaire ultraviolette photodissocie la vapeur d'eau surtout dans la thermosphère, cette molécule est en fait soumise à la dissociation dans la stratosphère et la mésosphère surtout par un processus d'oxydation très rapide avec des atomes excités résultant de la photodissociation de l'ozone. Un tel processus d'oxydation conduit à la disparition partielle du méthane et de la molécule d'hydrogène dans la stratosphère à un point tel qu'il existe une déficience totale à la stratopause que le transport par diffusion turbulente ne peut compenser.

Les molécules d'hydrogène sont en fait produites au sein de la mésosphère et en particulier à la mésopause par la réaction entre HO_2 et H. L'hydrogène qui est un catalyseur dans son action de destruction des atomes d'oxygène conduit ainsi à une diminution de la concentration d'ozone, en particulier dans la mésosphère, par rapport à sa concentration dans une atmosphère d'oxygène pur. Elle est diminuée d'un facteur 1,5 au niveau de la stratopause et est réduite à 1/100 à la mésopause.

Par suite des réactions rapides entre OH et HO_2 amenant à sa reformation rapide, la vapeur d'eau maintient aisément sa distribution normale dans la stratosphère et la mésosphère. Quant à l'effet de la photodissociation directe dans la thermosphère, il est fortement compensé par le transport de la vapeur d'eau par diffusion turbulente. En tout cas, l'hydrogène s'échappant de la thermosphère est facilement compensé par la diffusion.

Diverses réactions dans lesquelles sont impliqués l'oxyde et le peroxyde d'azote doivent être introduites pour l'étude aéronomique des rapports des concentrations de OH et de HO_2 dans la stratosphère. D'ailleurs, leur effet se manifeste sur le comportement de l'eau oxygénée. Il semble bien que le rôle de telles réactions est de produire en particulier l'acide nitrique qui par son passage dans la troposphère est ainsi la cause de la disparition de l'oxyde d'azote produit au-delà de 120 km dans la thermosphère.

Samenvatting

In de thermosfeer en de opperste mesosfeer wordt, onder invloed van de zonnestraling, waterdamp ontbonden in waterstofatomen en hydroxylgroepen. In de stratosfeer en de lagere mesosfeer wordt H_2O voornamelijk ontbonden door een vlugge oxydatie ten gevolge van botsingen met aangeslagen zuurstofatomen die ontstaan door fotolyse van ozon. Deze botsingen verhinderen het bestaan van normale mengverhoudingen voor methaan en moleculaire zuurstof aan de stratopauze en wel in zulke mate dat de verdwijning van deze bestanddelen de toevoer uit lagere gebieden overtreft.

In de mesosfeer en in het bijzonder aan de mesopauze ontstaan de waterstofmolecules ten gevolge van opeenvolgende scheikundige reacties tussen HO_2 en H. De waterstof treedt op als catalysator bij de verwijdering van de zuurstofatomen waardoor de ozonconcentratie drastisch afneemt in de mesosfeer in vergelijking met deze in een exclusieve zuurstofatmosfeer, nl. met een factor 1,5 ter hoogte van de stratopauze tot ongeveer een factor 100 aan de mesopauze. De verticale verdeling van waterdamp in de stratosfeer en de mesosfeer wordt niet beïnvloed door dit ontbindingsproces aangezien hij vlug terug gevormd wordt.

Wervelingen in de thermosfeer zorgen er voor dat waterdamp het gebied bereikt waar fotolyse plaats heeft en wel zo dat de ontsnappende waterstof in voldoende mate aangevuld wordt.

Verschillende reacties waarbij NO en NO_2 betrokken zijn moeten gevoegd worden bij de reacties in de stratosfeer. Deze moleculen spelen een aeronomische rol bij de bepaling van de verhouding tussen de concentraties van OH en HO_2. Niettegenstaande de aanhoudende vorming van H_2O_2 moleculen is hun concentratie eerder gering. Men onderstelt dat de reacties, waarbij NO en NO_2 betrokken zijn, door de vorming van salpeterzuur tot de vernietiging van waterstofperoxyde leiden evenals tot de verdwijning van NO, die boven de 120 km in de thermosfeer gevormd wordt.

Zusammenfassung

In der Thermosphäre und in der höheren Mesosphäre dissoziert die Sonnenstrahlung Wasserdampf in Wasserstoff und in OH Radikalen. In der Stratosphäre und niedrigen Mesosphäre, ist H_2O meinstens durch Stossvorgänge mit Sauerstoff Atomen, die aus der Ozon Photodissoziation kommen, dissoziert. Durch diese Stossvorgänge kann kein normales Mischungsverhältnis für Methan und Molekularwasserstoff zur Stratopause stattfinden. Die senkrechte Eddydiffusion ist nicht stark genug, um ein normales Mischungsverhältnis aufzubilden.

Molekularwasserstoff wird in der Mesosphäre und besonders zur Mesopause durch Reaktionen zwischen HO_2 und H verursacht. Wasserstoff wirkt als einen Katalysator für die Vernichtung der Sauerstoff Atomen und vermindert auf dieser Weise die Ozondichte, besonders in der Mesosphäre. Die Ozondichte ist bei einem Faktor 1,5 zur Stratopause und 100 zur Mesopause vermindert. Die senkrechte Wasserdampfverteilung ist, in der Stratosphäre und in der Mesosphäre, durch die Dissoziation nicht verändert, da die Wiederbildung, sehr rasch ist. In der Thermosphäre ist die Photodissoziation durch Eddydiffusionstransport von Wasserdampf ausgegleicht.

Verschiedene Reaktionen, worin Stickstoffoxide und Stickstoffperoxide eine Rolle spielen, sind sehr wichtig für die Feststellung der Verhältnisse von OH und HO_2 in der Stratosphäre. Ihre Einwirkung zeigt sich auch beim Wasserstoffperoxide Vertragen. Solche Reaktionen führen wahrscheinlich zur Bildung der Stickstoffsäuren, die auf dieser Weise für das Verschwinden der oberhalb 120 km gebildeten Stickstoffoxide verantwortlich sind.

I. INTRODUCTION. DISSOCIATION OF H_2O, CH_4 and H_2

Vibrational-rotational bands of the hydroxyl radical OH, which appear in the airglow aroused interest in the photochemistry of hydrogen-oxygen compounds [BATES and NICOLET, 1950 a; HERZBERG, 1951] and, in particular of methane [BATES and NICOLET, 1950 b; BATES and WITHERSPOON, 1952] and of water vapor [BATES and NICOLET, 1950 c] twenty years ago.

The water vapor which is quite abundant near ground level with a fractional volume concentration reaching 10^{-2}, decreases in mixing ratio with altitude. 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] in the stratosphere. Methane and molecular hydrogen, which have been found as permanent constituents of the troposphere have continuous sources at ground level. Their total amounts by volume are, respectively, 1.5×10^{-6} and 0.5×10^{-6} of the major gases N_2 and O_2. Unlike water vapor, however, their fractional concentrations are not affected through the troposphere. Consequently, above the tropopause, the combined H-atom content in CH_4 is identical with the adopted content in H_2O. Thus, the total amount of free hydrogen cannot be far from 10^{-5}.

Water vapor can be dissociated by sunlight (Figure 1) and its photodissociation coefficient at 100 km is only

$$J_{H_2O} (\lambda > 1750 \text{ A}) = 1.7 \times 10^{-6} \text{ sec}^{-1}, \tag{1}$$

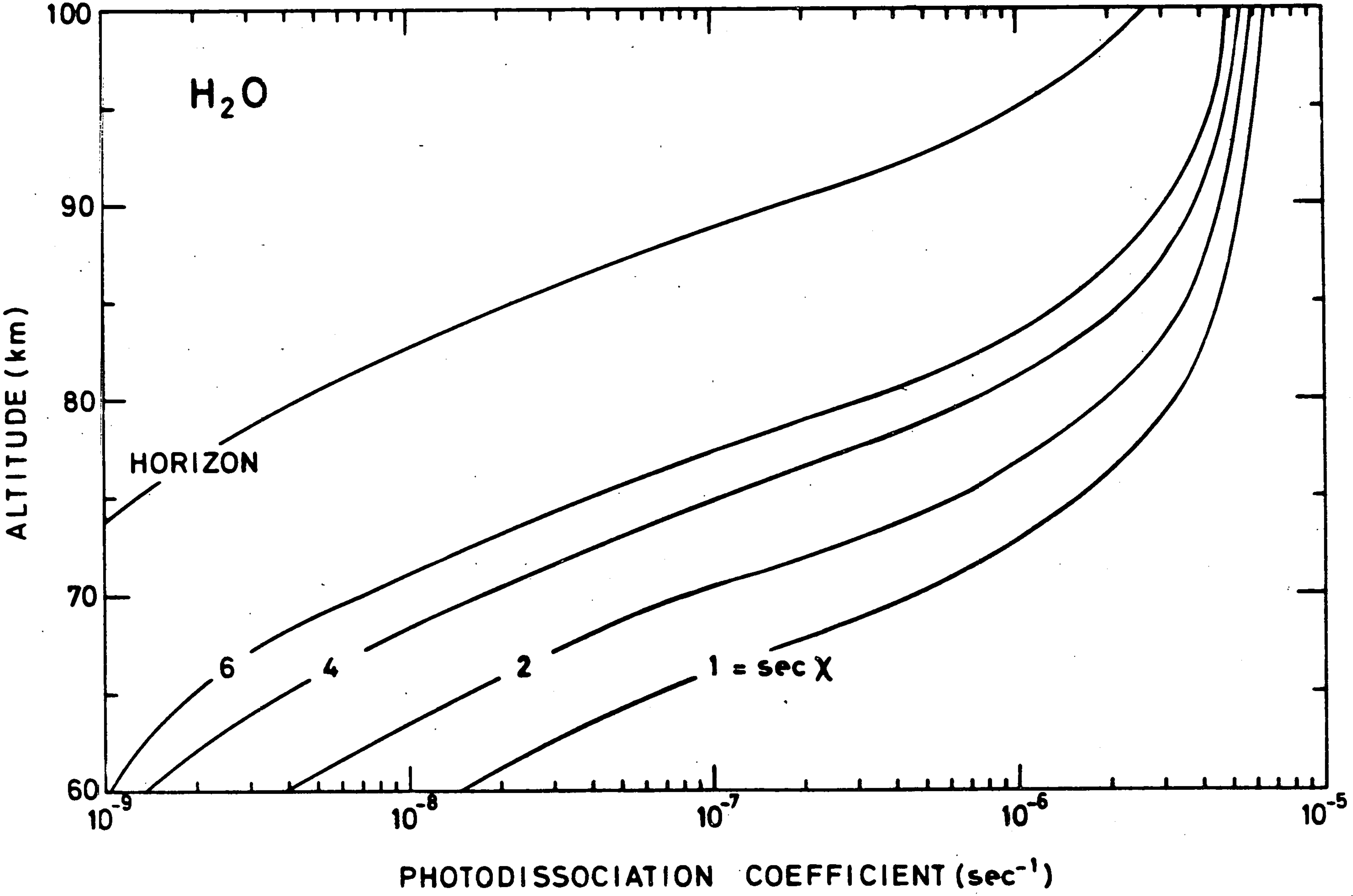

FIGURE 1

Photodissociation coefficient (sec^{-1}) of water vapor in the lower thermosphere and mesosphere for various solar zenith angles. Overhead sun, sec $\chi = 1$; sec $\chi = 2$, 4 and 6 and sun at the horizon.

and at the mesopause level, 85 km,

$$J_{H_2O}(\lambda > 1750 \text{ A}) = 1 \times 10^{-6} \text{ sec}^{-1} . \quad (2)$$

The radiation (see Figure 2) which is not attenuated reaches the lower mesosphere, and at 65 km the photodissociation coefficient is

$$J_{H_2O}(\lambda > 1750 \text{ A}) = .5 \times 10^{-7} \text{ sec}^{-1} . \quad (3)$$

But, an important part of the photodissociation of H_2O in the upper mesosphere and in the lower thermosphere is due to Lyman-α which can reach the 70 km level as indicated in Figure 2. The process

$$H_2O + h\nu \ (\lambda = 1216 \text{ A}) \rightarrow H(^2S) + OH\ (^2\Sigma)_{v' \leq 2} \quad (4)$$

is possible, since an experimental analysis [CARRINGTON, 1964] shows that the fluorescence process of the OH bands is between 1 and 10% of the total process. Thus, a fluorescence of OH bands at 3064 A occurs in the upper mesosphere and lower thermosphere.

Methane can be also dissociated by sunlight. However, since the absorption cross section is very small at $\lambda > 1500$ A, the aeronomic photodissociation of CH_4 arises from Lyman-α with photodissociation coefficient at zero optical depth

$$J_{CH_4} (\lambda = 1216 \text{ A}) = 5 \times 10^{-6} \text{ sec}^{-1}. \quad (5)$$

The photodissociation coefficient is a decreasing function of the optical depth in the mesosphere and is negligible in the lower mesosphere (Figure 3).

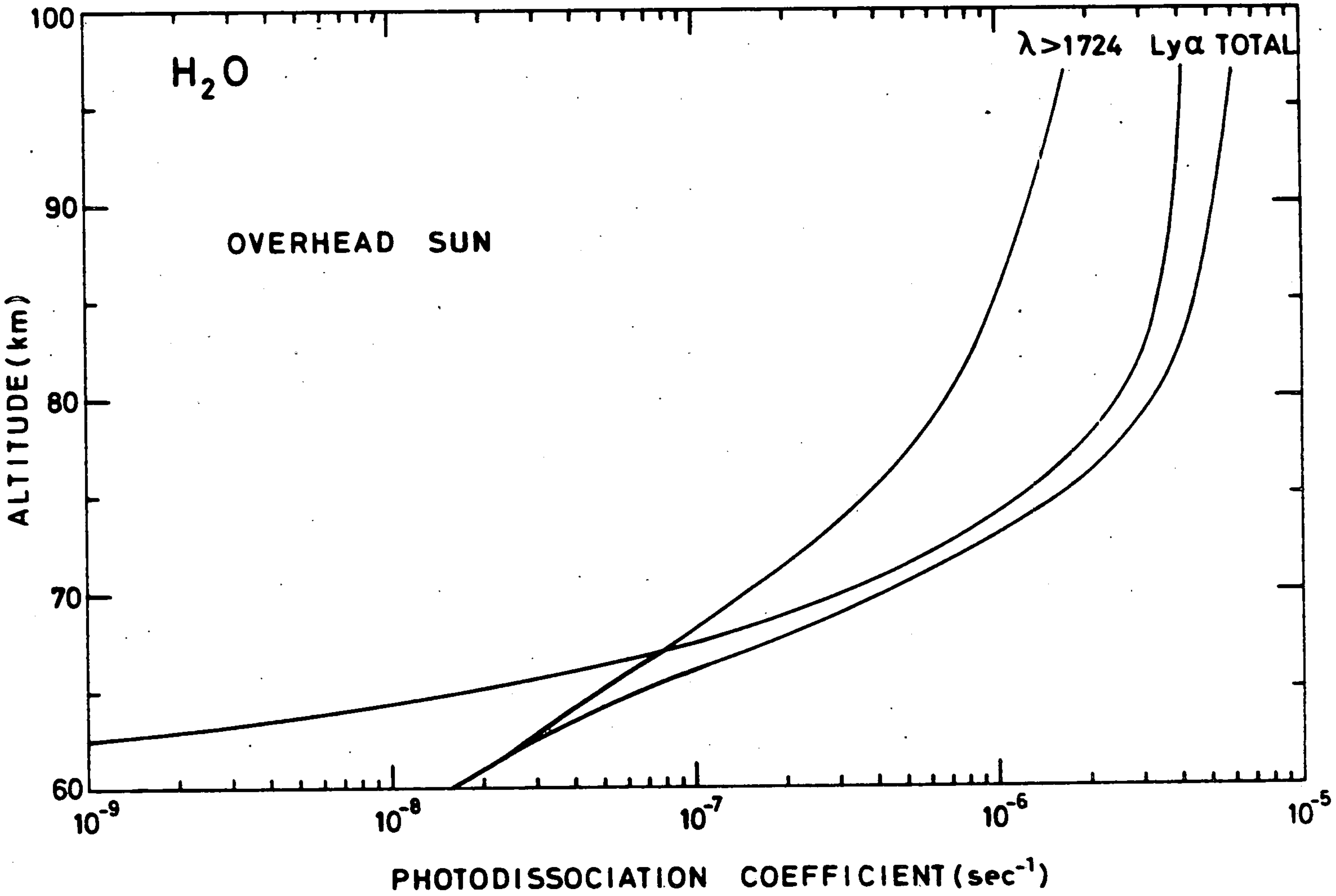

FIGURE 2

Photodissociation coefficient of water vapor for radiation of $\lambda > 1724$ A and for Lyman α. The dissociation near the mesopause level is principally due to Lyman α.

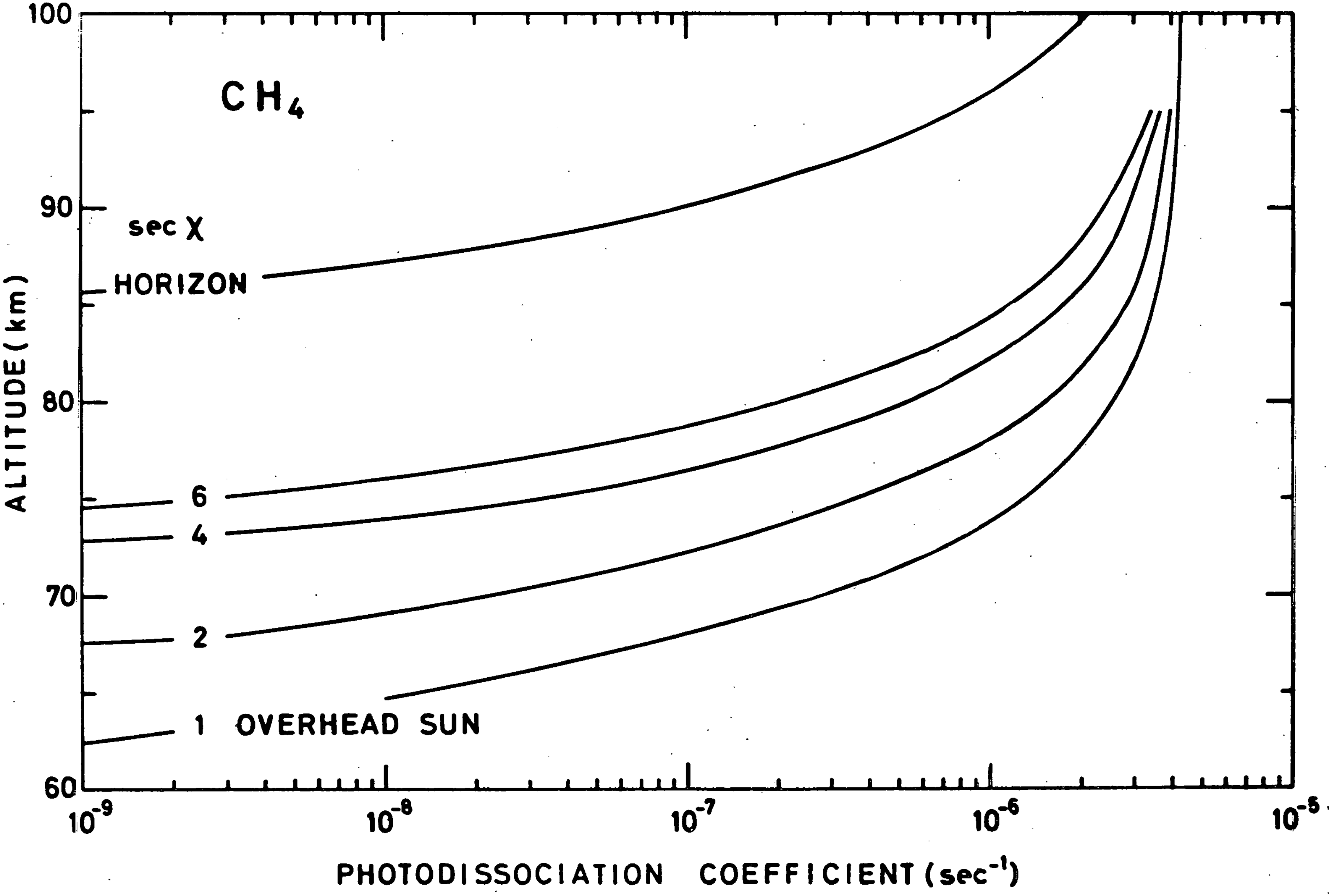

FIGURE 3

Photodissociation coefficient of methane in the lower thermosphere and mesosphere for various solar zenith angles by solar radiation at Lyman-α. Overhead sun, sec $\chi = 1$; sec $\chi = 2$, 4 and 6 and sun at the horizon ($\chi = 90°$).

Among the other hydrogen oxides which may be present in the upper atmosphere, HO_2 and H_2O_2 can be subject to photodissociation. 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 (see Figure 4)

$$J_{H_2O_2} = 1.2 \times 10^{-4} \text{ sec}^{-1} \quad . \tag{6}$$

The photolysis of H_2O_2 cannot occur in the far ultraviolet and below 2100 A the photodissociation coefficient is less than 10^{-5} sec^{-1}. Therefore the fluorescence of OH bands cannot be an important aeronomic process.

Photodissociation is not the only disruptive process of H_2O, CH_4 and H_2O_2. Among the primary processes likely to be important, the reaction with atomic oxygen must be considered since $O(^3P)$ atoms exist in a sunlit atmosphere where ozone is present. However, all reactions are endothermic; the oxidation of water vapor is impossible and that of methane and molecular hydrogen requires an activation energy between 8 and 10 kcal/mole.

Considering that atomic oxygen can be in the excited ^1D state, other reactions are possible in the stratosphere and mesosphere [CADLE, 1964]. Recent experimental evidence [DEMORE and RAPER, 1967; DEMORE, 1967a; ENGLEMAN, 1965] indicates that the rate coefficients of oxidizing reactions with $O(^1D)$ atoms are of the order of 10^{-10} cm^3 sec^{-1}. The following reactions occur in the stratosphere

$$O(^1D) + H_2 \rightarrow H + OH^* \, (v \leq 4) + 43.5 \text{ kcal} \tag{7}$$

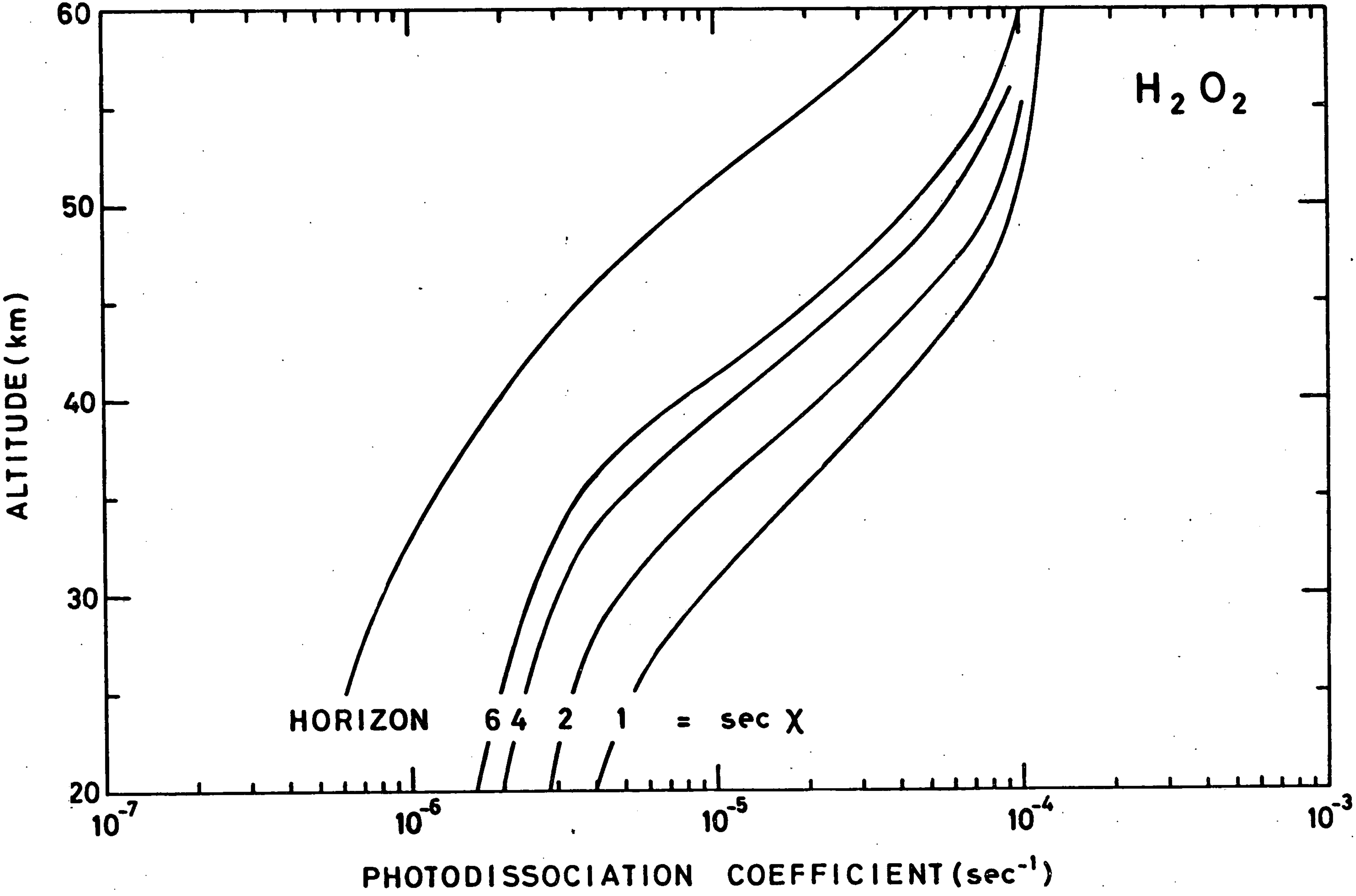

FIGURE 4

Photodissociation coefficient of hydrogen peroxide in the mesosphere and stratosphere for various solar zenith angles.

$$O(^1D) + CH_4 \rightarrow CH_3 + OH^* \ (v \leq 4) + 43.5 \text{ kcal} \qquad (8)$$

$$O(^1D) + H_2O \rightarrow OH + OH^* \ (v \leq 2) + 28.8 \text{ kcal} . \qquad (9)$$

Thus, the presence of $O(^1D)$ atoms leads to the possibility of the production of hydrogen atoms by CH_4, H_2 and H_2O. With the fractional volume concentrations which have been adopted, the total production P(H) of hydrogen atoms is

$$P(H) = 13 \times 10^{-16} \ n(M) \ n[\ O(^1D)] \ \ cm^{-3} \ sec^{-1} \qquad (10)$$

if n(M) is the total concentration and if the average rate coefficient of 10^{-10} cm^3 sec^{-1} is adopted.

II. PRODUCTION OF EXCITED OXYGEN ATOMS

When an analysis of the ozone photodissociation is made, it is necessary to distinguish between the various products in order to show the production of excited atoms or molecules. In the spectral range of the Huggins bands, an unimportant process is

$$O_3 + h\nu \ (\lambda \leq 4125 \text{ A}) \rightarrow O_2 \, (^3\Sigma_g^-) + O(^1D) \qquad (11a)$$

but at shorter wavelengths an important process must be

$$O_3 + h\nu \ (\lambda \leq 3110 \text{ A}) \rightarrow O_2 \, (^1\Delta_g) + O(^1D). \qquad (11b)$$

An important experimental result [DEMORE and RAPER, 1966] is that at $\lambda < 3000$ A the photodissociation process leads to a complete production of $O(^1D)$ atoms and that at $\lambda = 3130$ A the $O(^1D)$ production is only 0.4 ± 0.15 of the total number of atoms. The total number of photodissociation processes of O_3 leading to $O(^1D)$ atoms is about 10^6 cm^{-3} sec^{-1} in the upper mesosphere and reaches a maximum of about 10^9 cm^{-3} sec^{-1} for an overhead sun below the stratopause (see Figure 5). The variation of the production of $O(^1D)$ atoms with the solar zenith angle is important and leads to a rapid decrease from the stratopause to the tropopause.

In order to determine the concentration of $O(^1D)$ atoms in a sunlit atmosphere it is necessary to introduce the effect of the principal loss processes, namely deactivation by N_2 and O_2. All experimental values [DEMORE and RAPER, 1964, SNELLING and BAIR, 1967; YOUNG and BLACK, 1967; YOUNG et al, 1969; NOXON, 1969] show that the quenching rate coeficient is greater than 10^{-11} cm^3 sec^{-1} and may reach 10^{-10} cm^3 sec^{-1}. The following working value for the whole homosphere is adopted here

$$k_Q\,(^1D, M) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \tag{12a}$$

which leads to

$$n[O(^1D)] = 2 \times 10^{10}\, n(O_3)\, J_3\,(^1D) \,/\, n(M) \tag{12b}$$

where $n(O_3)\ J_3(^1D)$ is the production of $O(^1D)$ atoms illustrated in Figure 5. The photoequilibrium concentrations for various solar zenith angles are given in Table 1; the error involved should be less than 50%. A concentration peak less than 10^3 cm^{-3} occurs near the stratopause for an overhead sun. Concentrations of $O(^1D)$ greater than 10^3 cm^{-3} are not possible.

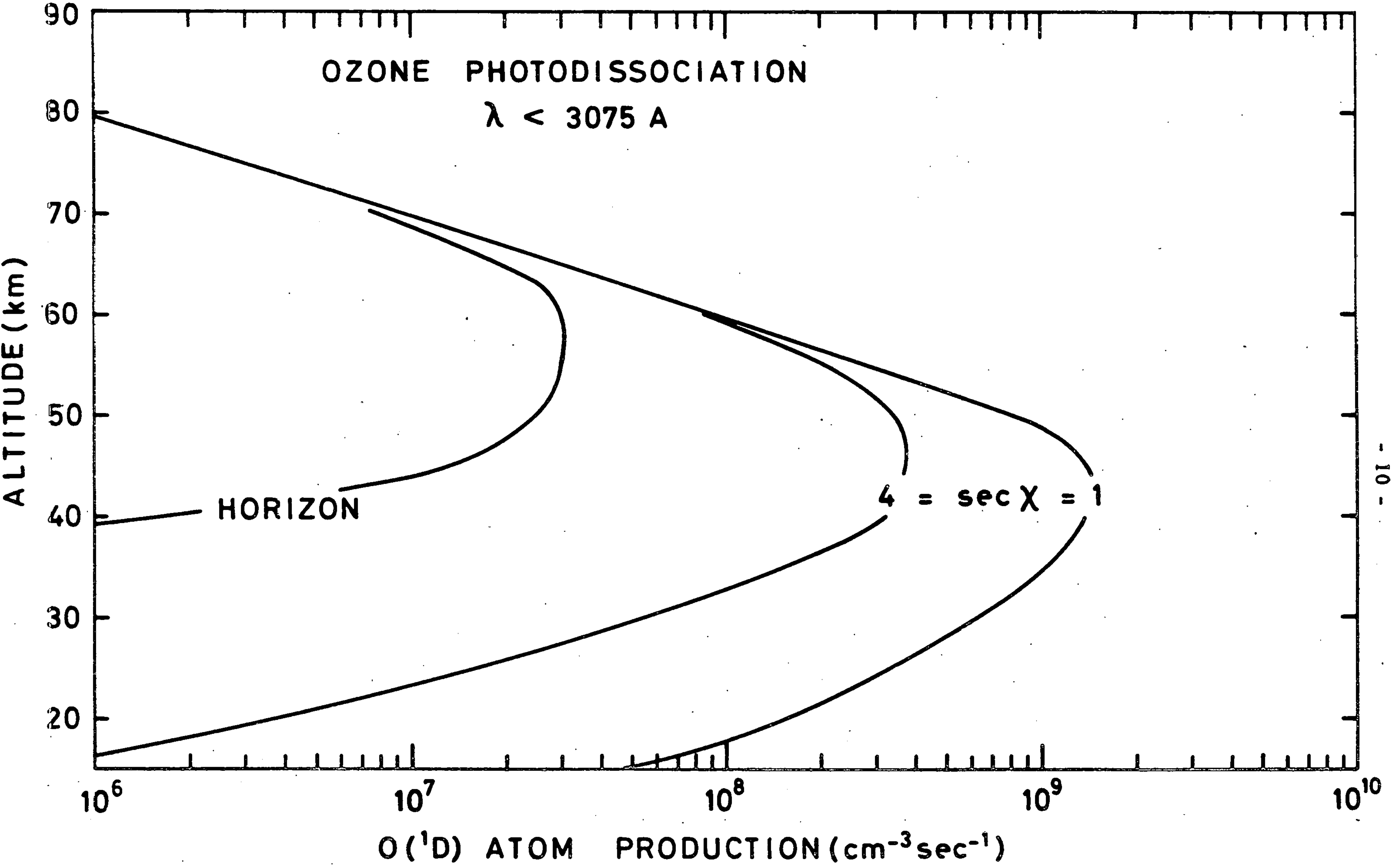

FIGURE 5

Production of O(^{1}D) atoms by the ozone photodissociation for various solar zenith angles. Overhead sun, sec $\chi = 1$; sec $\chi = 4$; sun at the horizon, $\chi = 90^\circ$.

TABLE 1

Concentration of $O(^1D)$ in a Sunlit Atmosphere
Equilibrium Conditions

Altitude (km)	$\sec\chi = 1$ (cm^{-3})	$\sec\chi = 2$ (cm^{-3})	$\sec\chi = 4$ (cm^{-3})	$\sec\chi = 6$ (cm^{-3})	Horizon (cm^{-3})
20	2.5	0.6	5.6	6.2	-
25	1.1×10^{1}	3.2	5.1×10^{-1}	1.0×10^{-1}	-
30	4.4×10^{1}	1.6×10^{1}	4.0	1.4	2.7×10^{-9}
35	1.5×10^{2}	6.6×10^{1}	2.4×10^{1}	1.1×10^{1}	4.0×10^{-4}
40	4.4×10^{2}	2.1×10^{2}	9.9×10^{1}	5.9×10^{1}	5.2×10^{-1}
45	7.8×10^{2}	4.3×10^{2}	2.1×10^{2}	1.4×10^{2}	8.0
50	7.9×10^{2}	6.0×10^{2}	3.8×10^{2}	2.6×10^{2}	2.7×10^{1}
55	5.6×10^{2}	5.1×10^{2}	4.3×10^{2}	3.6×10^{2}	5.7×10^{1}
60	3.3×10^{2}	3.2×10^{2}	3.0×10^{2}	2.9×10^{2}	1.0×10^{2}
65	2.0×10^{2}	1.9×10^{2}	1.9×10^{2}	1.9×10^{2}	1.3×10^{2}
70	1.2×10^{2}	1.2×10^{2}	1.2×10^{2}	1.2×10^{2}	1.0×10^{2}

At the mesopause, the concentration of $O(^1D)$ atoms begins to increase again due to the photodissociation of O_2 in the Schumann-Runge continuum. For an overhead sun the following concentrations are obtained:

Altitude (km)	95	100	105	110	115	120
Concentration $O(^1D)$ (cm^{-3})	4×10^{2}	10^{3}	2×10^{3}	4×10^{3}	5×10^{3}	4×10^{3}

As far as the $O(^1S)$ atoms are concerned, their low collisional deactivation with N_2 [STHUL and WELGE, 1969]

$$k_Q(^1S, N_2) < 5 \times 10^{-17}\ \text{cm}^3\ \text{sec}^{-1} \qquad (13a)$$

and their moderate deactivation by O_2 [STHUL and WELGE, 1969; BLACK et al, 1969]

$$k_Q(^1S, O_2) = 3 \text{ to } 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \tag{13b}$$

lead to equilibrium conditions written as follows:

$$n[O(^1S)] = 10^{13}\, n(O_3)\, J_3\, (^1S)/n(M) \; . \tag{13c}$$

Thus, equations (12b) and (13c) lead to

$$\frac{n[O(^1S)]}{n[O(^1D)]} = \frac{5 \times 10^2\, J_3\, (^1S)}{J_3\, (^1D)} \tag{14}$$

Numerical results for an overhead sun are given in the following table:

Altitude (km)	100	50	30
$J_3\ (^1S)$ (sec^{-1})	3.5×10^{-6}	2.7×10^{-6}	3.0×10^{-7}
$J_3\ (^1D)$ (sec^{-1})	8.6×10^{-3}	3.4×10^{-3}	2.1×10^{-4}
$n[O(^1S)]/n[O(^1D)]$	0.20	0.40	0.71

From that table in which $J_3(^1S)$ is the maximum possible value it is clear that the concentrations of the ^1S oxygen atoms produced by the ozone photodissociation are a fraction of that of the ^1D oxygen atoms. An oxidizing reaction with $O(^1S)$ atoms requires a rate coefficient greater than rate coefficients with $O(^1D)$ in order to be compared with (7), (8) and (9). This may happen for water vapor but not for molecular hydrogen [STHUL and WELGE, 1969].

III. STRATOSPHERIC CONDITIONS

From the foregoing discussion it is apparent that the dissociation mechanism of H_2O, CH_4 and H_2 in the stratosphere is an oxidation process by ^1D oxygen atoms. However, the vertical distribution of H_2, CH_4 and H_2O in the stratosphere can be maintained by atmospheric mixing only if the oxidation process is a very slow reaction [BATES and NICOLET, 1965].

In the presence of eddy diffusion, the vertical speed w_1 of constituent of scale height H_1 can be written as follows [NICOLET, 1968]

$$w_1 = \frac{D_e}{H} \left[\frac{H}{H_1} - 1 \right] \qquad (15)$$

in which D_e is the eddy diffusion coefficient and H is the atmospheric scale height. The diffusive upward current of CH_4 molecules is, therefore, given by

$$F_{CH_4} = n(CH_4)\, w_{CH_4} \qquad (16)$$

and must correspond to about

$$F_{CH_4} = \frac{1}{2}\, a^*_{0-CH_4}\, n^*(^1D)\, n_{CH_4}\, H_{CH_4} \qquad (17)$$

in order to replace the methane which is destroyed chemically in a sunlit atmosphere by reaction with excited oxygen atoms. Using numerical values in (16) and (17) it is found that eddy diffusion is necessary to maintain CH_4 molecules in the stratosphere.

If the ratio of the local scale height $H(CH_4)/H(M) = 1/2$ it is found that an eddy diffusion coefficient greater than 10^4 cm^2 sec^{-1} is required near the stratopause (cf Figure 6). Furthermore, a mixing distribution of CH_4, i.e. a scale height, $H = 1.1\ H(CH_4)$ implies a permanent eddy diffusion coefficient greater than 10^5 cm^2 sec^{-1} (Fig. 6). It seems, therefore, that it is extremely difficult to maintain a constant mixing ratio of methane in the stratosphere.

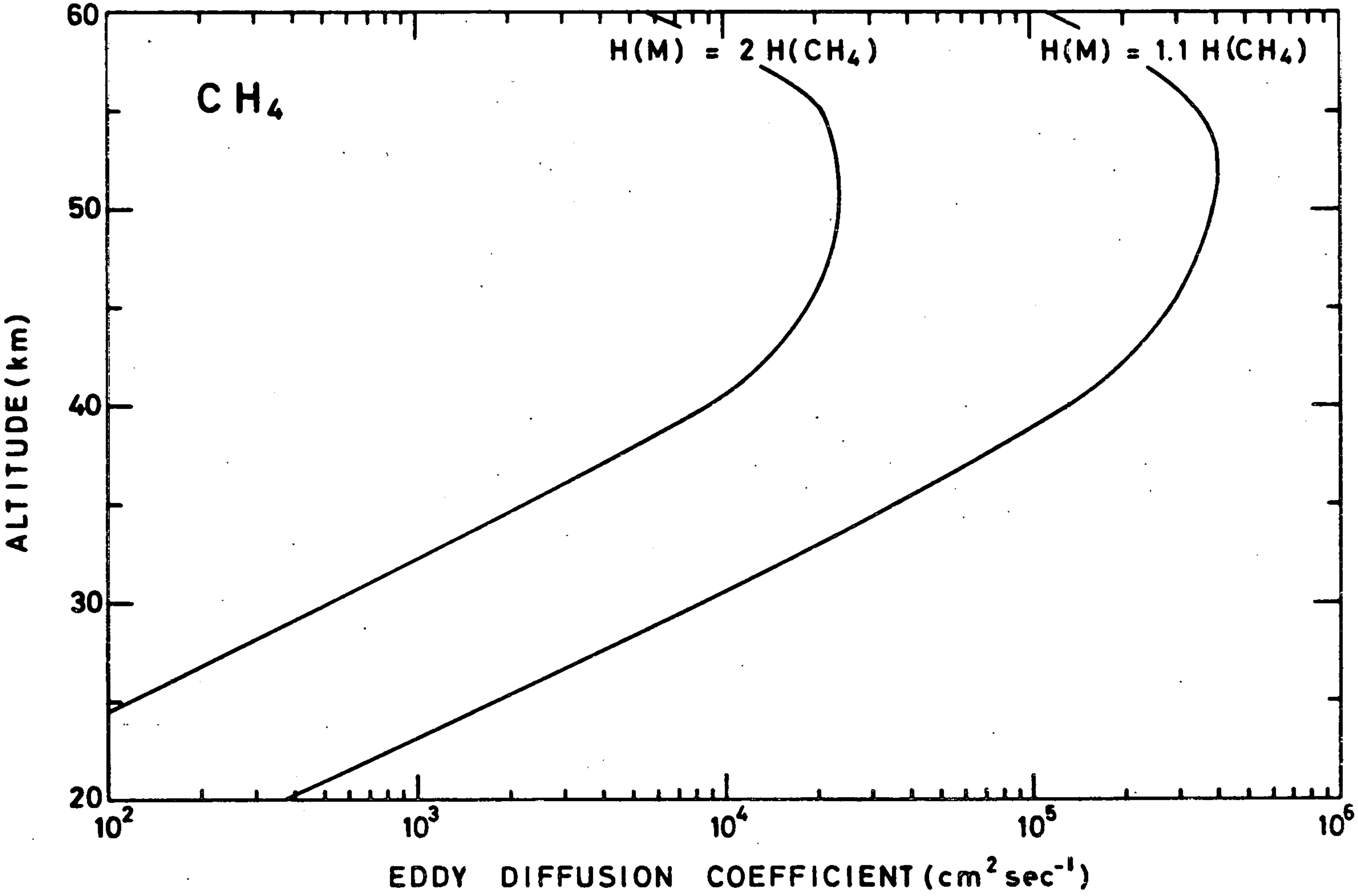

FIGURE 6

Eddy diffusion coefficient necessary to maintain methane in the stratosphere with scale height H(CH4) = 0.5 H(M) and H(CH4) = 0.9 H(M), respectively; H(M) is the local atmospheric scale height. Methane is oxidized by excited atoms O(^{1}D).

By an argument similar to that used in connection with the distribution of methane, it may be found that H_2 undergoes the same processes (Figure 7). It is clear also that the removal of a single atom of H_2O through a reaction with an excited oxygen atom leads to a dissociation of the molecule at a rate which has a peak in the upper stratosphere. Numerical results corresponding to $H = 2\ H(H_2O)$ and $H = 1.1\ H(H_2O)$ are illustrated in Figure 8 where eddy diffusion coefficients at the stratopause should be not less than 10^4 cm^2 sec^{-1} and 10^5 cm^2 sec^{-1}, respectively. In the mesosphere, where the photodissociation of water vapor occurs, it is clear that the eddy diffusion must go up to 5×10^6 cm^2 sec^{-1} to maintain a mixing distribution at the mesopause.

Since it is extremely difficult to assume that permanent eddy diffusion coefficients are more than 10^5 cm^2 sec^{-1} in the upper stratosphere, a decrease of the ratios $n(H_2)/n(M)$ and $n(CH_4)/n(M)$ must be considered in the stratosphere. It seems, therefore, that one may assume that in the region below 35 km, H_2 and CH_4 are oxidized and lead to H_2O, introducing the possibility of an increase in the mixing ratio $n(H_2O)/n(M)$. The behavior of water vapor is completely different from that of methane and molecular hydrogen for which there is no possibility of immediate re-formation after the attack by the oxidation processes.

All products of the oxidation and dissociation of H_2, CH_4 and H_2O lead to the formation of water vapor through atomic hydrogen, hydroxyl and hydroperoxyl radicals. When a uniform mixing is accepted for H_2O in the stratosphere, the hypothesis is made that water vapor is involved in a sufficiently rapid catalytic action so that an anomalously high eddy diffusion coefficient ($>10^5$ cm^2 sec^{-1} at the stratopause, cf Figure 8) is not required. At the mesopause and in the lower thermosphere,

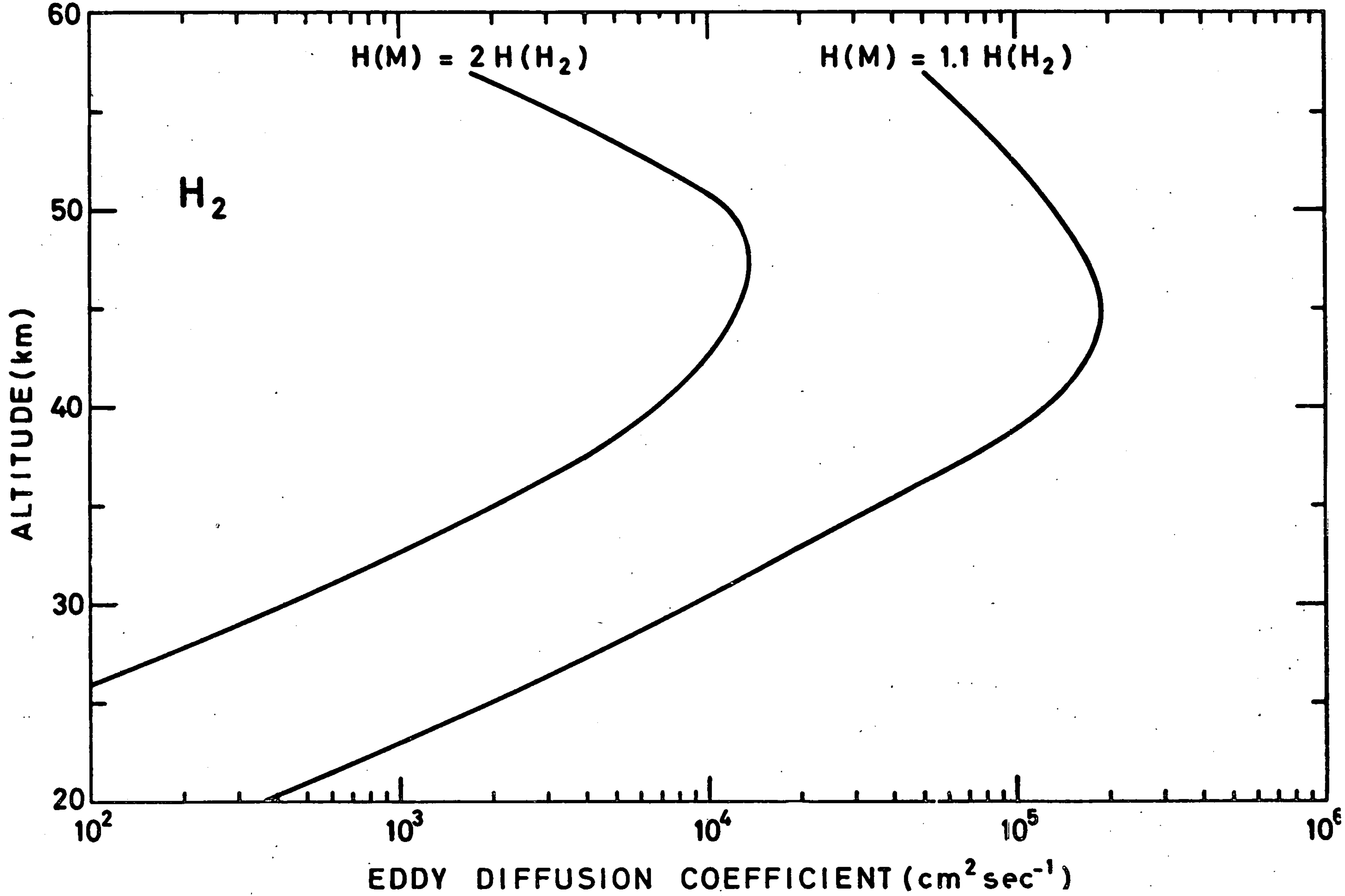

FIGURE 7

Eddy diffusion coefficient necessary to maintain molecular hydrogen in the stratosphere with a scale height $H(H_2) = 0.5\ H(M)$ and $H(CH_2) = 0.9\ H(M)$, respectively; H(M) is the local atmospheric scale height. H_2 is destroyed by $O(^1D)$.

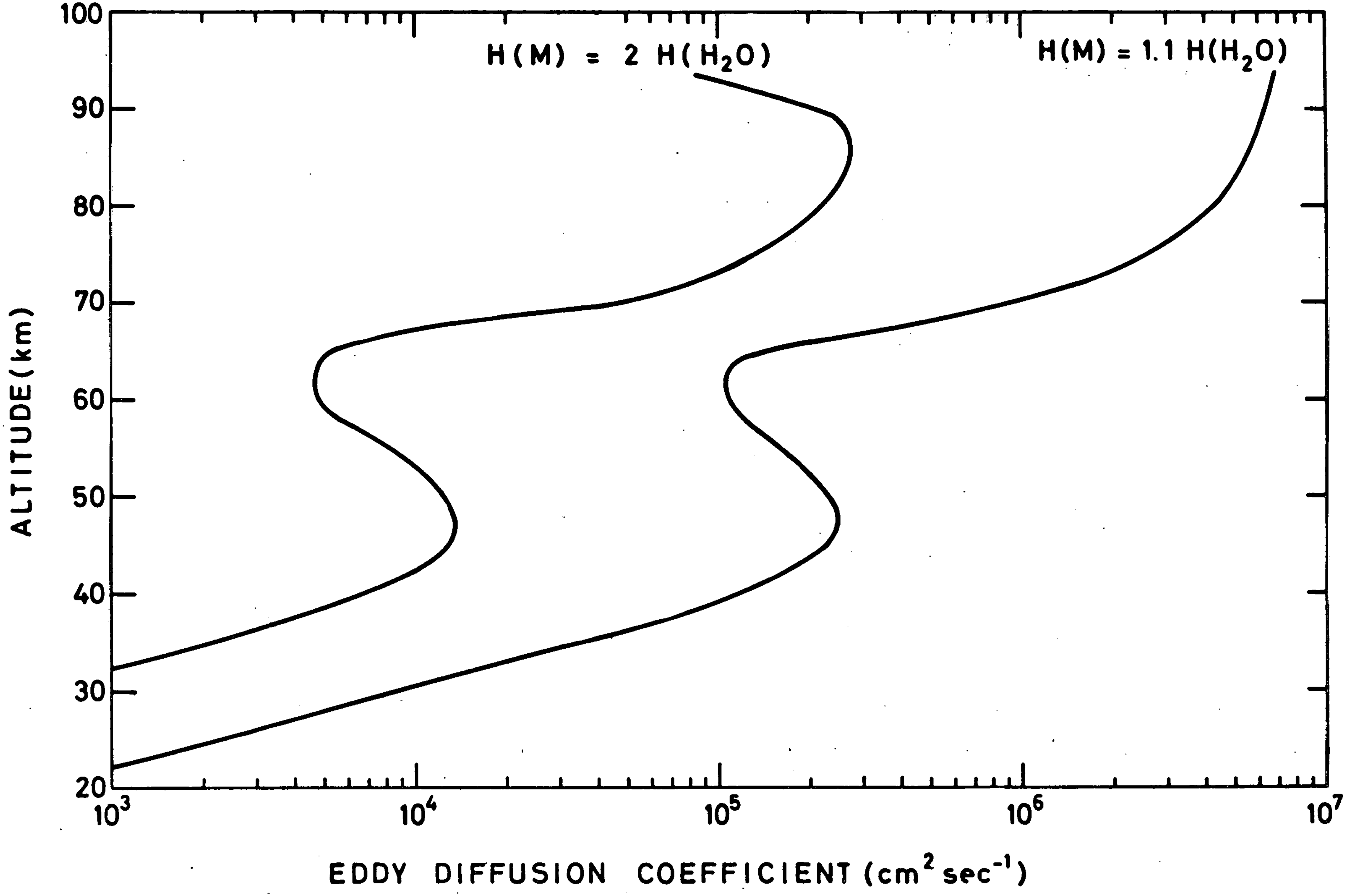

FIGURE 8

Eddy diffusion coefficient which would be necessary to maintain water vapor from the stratosphere to lower thermosphere with no re-formation process of H_2O; $H(M) = 2\ H(H_2O)$ and $H(M) = 1.1\ H(H_2O)$ correspond to the local atmospheric scale height and the assumed water vapor scale height.

where the H_2O re-formation is slow, the eddy diffusion leads to a vertical transport of H_2O molecules from the mesosphere.

IV. HYDROGEN-OXYGEN ATMOSPHERE

In order to describe a hydrogen-oxygen atmosphere in a simple way, it is necessary to eliminate the less probable reactions, [NICOLET, 1966].

The principal reactions between atomic hydrogen, hydroxyl and hydroperoxyl radicals in an ozone-atomic oxygen atmosphere are shown in Figure 9. It is clear that the atomic hydrogen concentration must increase with the atomic oxygen concentration and that the hydroperoxyl radical concentration increases with the ozone concentration.

A simple expression for the ratio n(OH)/n(H) in the whole homosphere where an adequate number of oxygen atoms are present is

$$\frac{n(OH)}{n(H)} = \frac{a_1\, n(M)\, n(O) + a_2\, n(O_3)}{a_5\, n(O)} . \qquad (18)$$

In the same way the expression for the equilibrium ratio $n(HO_2)/n(H)$ is obtained

$$\frac{n(HO_2)}{n(H)} = \frac{a_1\, n(M)\, n(O_2)}{a_7\, n(O)} + \frac{a_6\, n(O_3)}{a_5\, n(O)} \times \frac{a_1\, n(M)\, n(O_2) + a_2\, n(O_3)}{a_7\, n(O)} . \qquad (19)$$

Expressions (18) and (19), assuming $a_5 = a_7$, lead to

$$\frac{n(HO_2)}{n(OH)} = \frac{a_1\, n(M)\, n(O_2)}{a_1\, n(M)\, n(O_2) + a_2\, n(O_3)} + \frac{a_6\, n(O_3)}{a_7\, n(O)} . \qquad (20)$$

$$O - OH - H - HO_2 - O_3$$

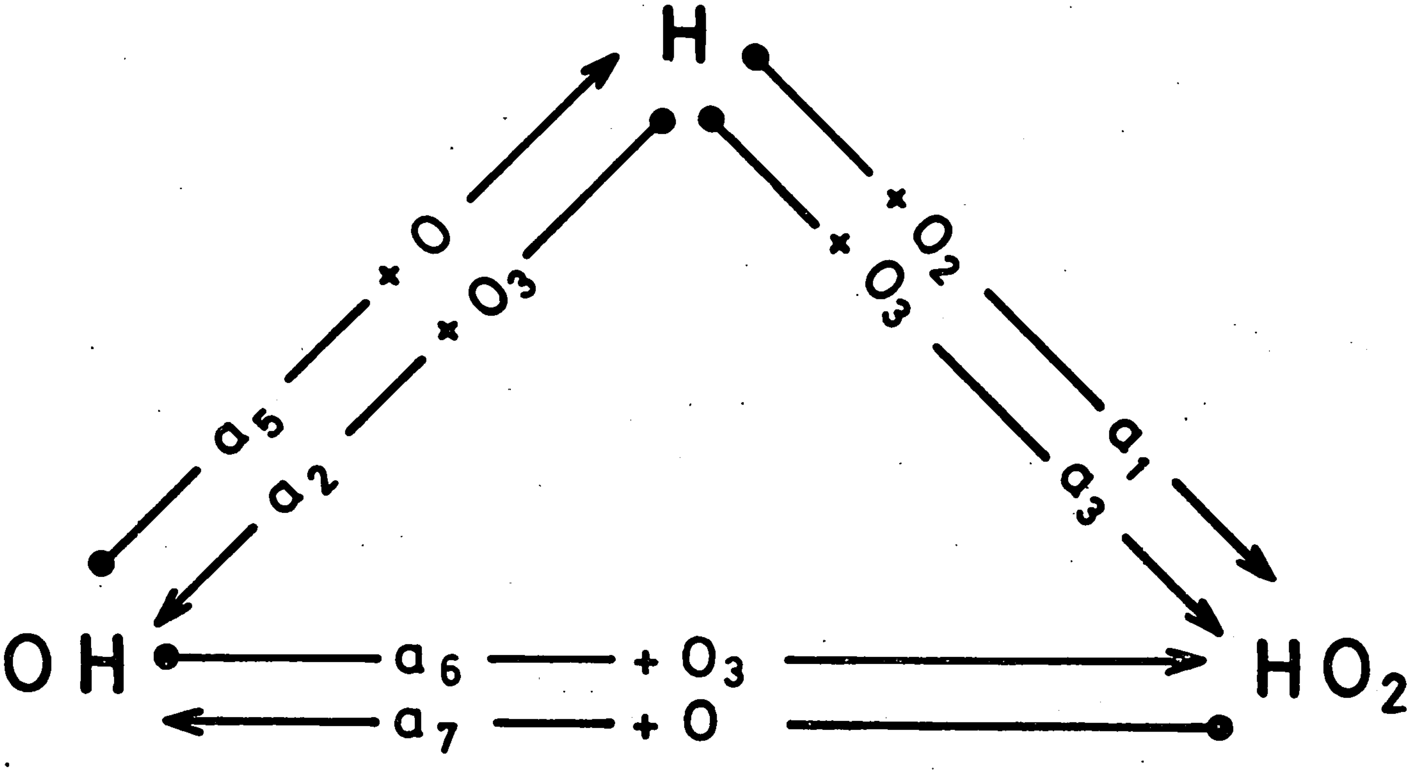

FIGURE 9

Principal reactions in which H, OH and HO_2 are involved with O and O_3.

In equations (18), (19) and (20), the three-body reaction of atomic hydrogen with molecular oxygen is of greater importance;

$$(a_1) \; ; \; H + O_2 + M \rightarrow HO_2 + M + 46 \text{ kcal} \qquad (21a)$$

has a rate coefficient [CLYNE and THRUSH; 1963b] which is taken for aeronomic purposes as

$$a_1 \, n(M) = 3.3 \times 10^{-33} e^{800/T} \, n(N_2, O_2) \text{ cm}^3 \text{ sec}^{-1}. \qquad (21b)$$

The other equally important loss process for atomic hydrogen is

$$(a_2) \; ; \; H + O_3 \rightarrow O_2 + OH^*_{v \leq 9} + 77 \text{ kcal} \qquad (22a)$$

for which a rate coefficient [PHILIPS and SCHIFF, 1962; KAUFMAN, 1964, 1969] with practically no activation energy is

$$a_2 = 1.5 \times 10^{-12} \, T^{1/2} \text{ cm}^3 \text{ sec}^{-1} . \qquad (22b)$$

Detailed studies have been made of the visible and infrared emission of this reaction in the laboratory [McKinley et al, 1955; GARVIN and McKINLEY, 1956; CAWTHON and McKINLEY, 1956; GARVIN, 1959; GARVIN et al, 1960 and 1962; BASS and GARVIN, 1962; ANLAUF et al, 1968].

The infrared chemiluminescence arising from this reaction [ANLAUF et al, 1968] indicates a vibrational distribution of OH^* with increasing populations up to $v'' = 9$ the highest possible level according to (22). The total emission rate in the night airglow must correspond to 5×10^{12} photons cm^{-2} [WALLACE, 1962] in the lower thermosphere and perhaps also in the upper mesosphere [PACKER, 1961] .

The production of hydroperoxyl radicals by

$$H + O_3 \rightarrow O + HO_2 + 22 \text{ kcal} \tag{23}$$

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

$$OH + O + M \rightarrow M + HO_2 + 63 \text{ kcal} \tag{24}$$

with a conventional value of the three-body rate coefficient a_4, are neglected compared with reaction (21).

The bimolecular process

$$(a_5);\ OH + O \rightarrow H + O_2 + 16.6 \text{ kcal} \tag{25a}$$

is an important reaction [CLYNE and THRUSH, 1963 a; KAUFMAN, 1964, 1969] with a rate coefficient

$$a_5 = 3 \times 10^{-12}\ T^{1/2}\ \text{cm}^3\ \text{sec}^{-1} \tag{25b}$$

leading to the value 5×10^{-11} cm^3 sec^{-1} at 0°C.

This reaction (25) in conjunction with (22) forms an important chain leading to the formation of oxygen molecules. In other words, atomic hydrogen acts as a catalyst for the destruction of odd oxygen atoms, and the atomic oxygen and ozone distributions are affected. The catalytic action of hydrogen is also of interest, in that it influences the nocturnal concentrations.

Other reactions involve hydroxyl radicals and ozone. The reaction

$$(a_6)\ ;\ OH + O_3 \rightarrow HO_2 + O_2 + 39 \text{ kcal} \tag{26a}$$

for which no direct measurement has been reported should have an upper limit of about 5×10^{-13} cm^3 sec^{-1} at room temperature [KAUFMAN, 1964, 1969]. With an activation energy of 4 kcal [BATES and NICOLET, 1950c], the following rate coefficient

$$a_6 = 1.5 \times 10^{-11} \, T^{1/2} \, e^{-2000/T} \, cm^3 \, sec^{-1} \tag{26b}$$

leads to 1.5×10^{-13} cm^3 sec^{-1} at the stratopause (270°K) and 5×10^{-15} cm^3 sec^{-1} at the tropopause (190°K) which is less than the value which has been used in various aeronomic calculations [HUNT, 1966 ; HESSTVEDT, 1968]. With a steric hindrance factor, it becomes

$$a_6 = 1.5 \times 10^{-12} \, T^{1/2} \, e^{-1500/T} \, cm^3 \, sec^{-1} \tag{26c}$$

which leads to 10^{-13} cm^3 sec^{-1} at the stratopause and 7.5×10^{-15} cm^3 sec^{-1} at the tropopause ; (26c) should be a maximum value. Neverless, such a reaction should be considered as a loss process of hydroxyl radicals; it has been introduced to explain the photolysis of ozone in the presence of water vapor. However, the following reaction between ozone and hydroperoxyl radicals has been also introduced in the OH-catalyzed chain decomposition of ozone

$$(a_{6c}); \; HO_2 + O_3 \rightarrow OH + 2O_2 + 31 \text{ kcal} \, . \tag{26}$$

There is no experimental evidence for such a reaction [DEMORE, 1967b] ; in any case its rate coefficient must be very small since such a reaction requires the simultaneous breakage of the bonds OH-O and O_2-O. The fact that OH radicals are involved in the catalyzed chain decomposition of O_3 in laboratory investigation is explained by the presence of vibrationally excited OH molecules which are a major reaction product [KAUFMAN, 1964; DEMORE, 1967b]. In stratospheric conditions, such OH^* excited molecules cannot play an active role and HO_2 as a chain carrier [HAMPSON, 1965; HUNT, 1966; HESSTVEDT, 1968; CRUTZEN, 1969] is therefore doubtful. In fact, the principal reaction leading to OH involved atomic oxygen [KAUFMAN, 1964].

$$(a_7);\ O + HO_2 \rightarrow O_2 + OH^*_{v \leq 6} + 55\ \text{kcal} \qquad (27a)$$

for which a rate coefficient

$$a_7 = 3 \times 10^{-12}\ T^{1/2}\ \text{cm}^3\ \text{sec}^{-1} \qquad (27b)$$

identical to a_5 is adopted in order to simplify the aeronomic analysis (cf equation 20), even if it is perhaps a factor of two too high [KAUFMAN, 1964].

It may be noted that reaction (27) may lead to excited OH molecules up to the level of vibrational quantum numbers $v \leq 6$ while reaction (22) can provide an energy to levels 7, 8 and 9 from which emission bands are observed in the airglow. Nevertheless, since atomic oxygen is an important minor constituent in the mesosphere, reaction (27) may lead to an additional emission of OH bands originating from levels of vibrational quantum number 6 or less, in the dayglow when atomic oxygen is present. It is expected, however, that deactivation processes of excited OH molecules are important in the middle and lower mesosphere. Reaction (22) leads to a peak in the lower themosphere where the night time emission is observed while (27) can play a role only below the mesopause.

Expressions (18) and (19) are obtained since it is assumed that

$$a_7\ n(O) > J_{HO_2} \qquad (28)$$

i.e. that the photodissociation coefficient of the hydroperoxyl radical is less important than the loss coefficient by reaction with atomic oxygen. Nothing is known about the photodissociation of the hydroperoxyl radical. Due to the similarity of the structure of HO_2 and that of hydrogen peroxide, for which $J_{H_2O_2} = 1.4 \times 10^{-4}$ sec^{-1} and also to the high photodissociation coefficient of nitrogen peroxide $J_{NO_2} = 3.5 \times 10^{-3}$ sec^{-1}, possible values such as

$$10^{-3} \leq J_{HO_2} \leq 10^{-4} \text{ sec}^{-1} \qquad (29)$$

can be suggested. Thus, the photodissociation could play a role on the ratio $n(OH)/n(HO_2)$ in the lower stratosphere.

V. AERONOMIC PROCESSES OF WATER VAPOR

After the photodissociation of water vapor in the mesosphere and lower thermosphere and the oxidizing reaction with $O(^1D)$ atoms (equation 9), the reactions between two hydroxyl radicals lead to its re-formation

$$(a_{16})\,;\ OH + OH \rightarrow H_2O + O + 17 \text{ kcal} \qquad (30a)$$

with an activation energy not greater than 2 kcal [KAUFMAN 1964, 1969; WESTENBERG and DE HAAS, 1965; WILSON and O'DONOVAN, 1967]. A minimum rate coefficient in the stratosphere and mesosphere will be given by

$$a_{16} = 5 \times 10^{-12}\, T^{1/2}\, e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1} . \qquad (30b)$$

In the same way, the reaction between hydroxyl and perhydroxyl radicals leads to H_2O [FONER and HUDSON, 1962; KAUFMAN, 1964]

$$(a_{17});\ OH + HO_2 \rightarrow H_2O + O_2 + 72 \text{ kcal} \tag{31a}$$

with perhaps a small activation energy (~ 1 kcal) to lead to a rate coefficient such as

$$a_{17} = 3 \times 10^{-13}\ T^{1/2}\ e^{-500/T}. \tag{31b}$$

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.

Another two-body process yielding hydrogen peroxide must be considered

$$(a_{27});\ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 + 42 \text{ kcal} \tag{32a}$$

for which we adopt [NICOLET, 1964] a rate coefficient which is similar to a_{16}

$$a_{27} = 5 \times 10^{-12}\ T^{1/2}\ e^{-1000/T}\ \text{cm}^3\ \text{sec}^{-1}. \tag{32b}$$

Inside the mesosphere and in the whole stratosphere, the following equation may be used

$$\frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + 2a_{16}\ n^2(OH) + 2a_{17}\ n(OH)\ n(HO_2) + 2a_{27}\ n^2(HO_2) = 2\ P(H) \tag{33}$$

where P(H) is the direct or indirect production of hydrogen atoms, and in order to simplify for an approximate calculation $a_{16} = a_{27} \doteq a_{17}/2$,

$$\frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + 2a_{16}\,[n(OH) + n(HO_2)]^2 = 2\,P(H). \tag{34a}$$

For night-time conditions (34a) becomes

$$\frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + 2a_{16}\,[n(OH) + n(HO_2)]^2 = 0 \tag{34b}$$

which shows that there is a nocturnal decay [NICOLET, 1964] of the OH and HO_2 concentrations in the stratosphere and mesosphere. At the mesopause level, the photodissociation of H_2O by Lyman-α is the principal production process. At lower altitudes the reaction of $O(^1D)$ atoms with H_2O and other hydrogen compounds is the source. Table II indicates the variation of the photodissociation coefficient of H_2O with altitude and the solar zenith angle. A complete knowledge (see Figure 8) of the vertical eddy diffusion coefficient is needed in order to determine the exact vertical distribution of H_2O. Values varying from 5×10^5 cm^2 sec^{-1} and 2×10^6 cm^2 sec^{-1} at 65 km to 7×10^6 cm^2 sec^{-1} have been assumed [HESSTVEDT, 1968]. If the vertical eddy diffusion coefficient is greater than 10^5 cm^2 sec^{-1}, it is certain (Figure 8) that the scale height of water vapor $H(H_2O) \geq \frac{1}{2}$ H the atmospheric scale height. Eddy diffusion coefficients between 10^6 and 10^7 cm^2 sec^{-1} indicate that $n(H_2O)/n(M)$ will not fall off sharply through the lower thermosphere.

TABLE II

Photodissociation Coefficient of Water Vapor by Lyman-α

Altitude (km)	$\sec\chi=1$ (sec^{-1})	Ratio $\sec\chi=4/\sec\chi=1$	Ratio $\sec\chi=6/\sec\chi=1$	Ratio Horizon/$\sec\chi=1$
90	4.0×10^{-6}	0.76	0.63	2.24×10^{-2}
85	3.5×10^{-6}	0.52	0.31	1.10×10^{-4}
80	2.6×10^{-6}	0.21	7.3×10^{-2}	6.8×10^{-10}
75	1.3×10^{-6}	2.7×10^{-2}	2.5×10^{-3}	-
70	3.0×10^{-7}	3.3×10^{-1}	1.6×10^{-8}	-
65	1.5×10^{-8}	-	-	-

In the lower mesosphere and stratosphere it is possible to deduce the photochemical conditions with (34). The essential result (see Table III) is that the time to reach the equilibrium (50% of the equilibrium concentration or from 50% to 80%) is less than three hours in the whole stratosphere and the mesosphere up to 70 km. Thus, H_2O can be kept in mixing conditions since loss and production processes of water vapor are sufficiently rapid. On the other hand, equilibrium conditions can be used to compute (see Table III) the total concentration $n(OH) + n(HO_2)$ which is not less than 10^7 cm^{-3} and reaches 10^8 cm^{-3} in the upper stratosphere. Numerical values which are given in Table III correspond to overhead sun conditions and different conditions are illustrated in Figure 10 where the concentrations correspond to various solar zenith angles. Variations in the stratosphere are particularly important in its lower part. Above 35 km the total concentration $n(OH) + n(HO_2)$ does not change very much except when the sun is near the horizon.

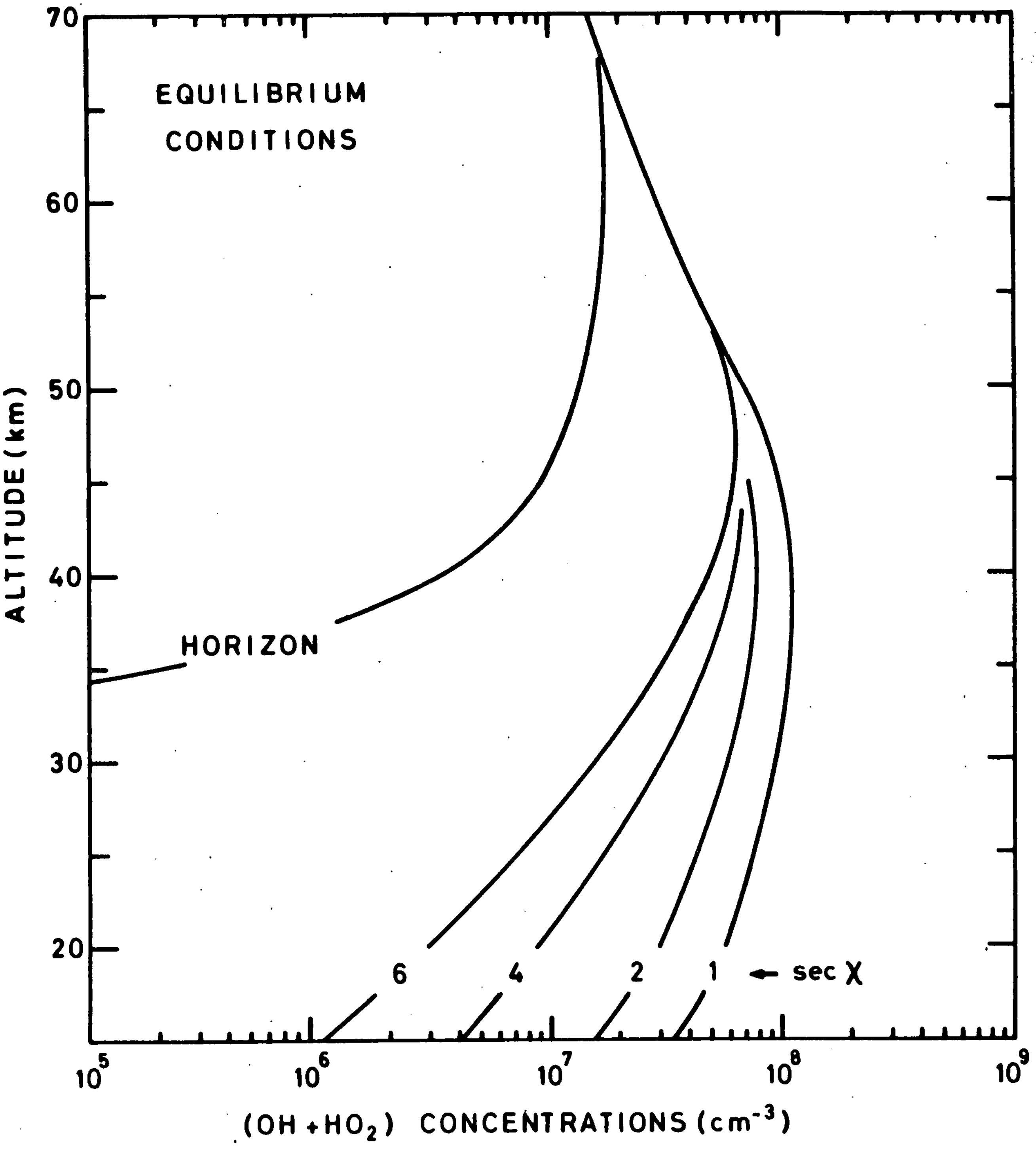

FIGURE 10

Total concentration of hydroxyl and hydroperoxyl radicals in the mesosphere and stratosphere for photoequilibrium conditions corresponding to various solar zenith angles. Overhead sun, sec χ = 1; sec χ = 2, 4 and 6; sun at the horizon, χ = 90°.

TABLE III

Production of OH and HO_2 by Oxidation of H_2O, (P), Total Concentration n(OH) + n(HO_2) for an Overhead Sun, and the Time to Reach 50% of the Equilibrium Value.

Altitude (km)	P (cm^{-3} sec^{-1})	n(OH) + n(HO_2) (cm^{-3})	Equilibrium Time (sec)
15	7.2×10^{2}	3.3×10^{7}	1.06×10^{4}
20	2.6×10^{3}	5.8×10^{7}	6.2×10^{3}
25	5.1×10^{3}	7.4×10^{7}	4.0×10^{3}
30	9.3×10^{3}	9.2×10^{7}	2.7×10^{3}
35	1.5×10^{4}	1.0×10^{8}	1.8×10^{3}
40	2.1×10^{4}	1.1×10^{8}	1.3×10^{3}
45	2.0×10^{4}	9.6×10^{7}	1.3×10^{3}
50	1.1×10^{4}	7.1×10^{7}	1.8×10^{3}
55	4.2×10^{4}	4.4×10^{7}	2.9×10^{3}
60	1.4×10^{3}	3.1×10^{7}	5.9×10^{3}
65	4.6×10^{2}	2.1×10^{7}	1.3×10^{4}
70	2.8×10^{2}	1.6×10^{7}	2.8×10^{4}

Thus, near 70 km, in the middle of the mesosphere where the following concentrations can be considered for an overhead sun: n(O) = 4×10^9 cm^{-3}; n(O_3) = 10^7; n(H) = 10^7; n(OH) = 10^7; n(HO_2) = 7×10^6, photochemical conditions seem to be well established. Below 40 km, however, it is difficult to determine the exact value of the ratio n(HO_2)/n(OH) since the reaction of HO_2 with O_3 is not well known. Furthermore, the effect of nitrogen oxides must be introduced.

VI. EFFECT OF NITROGEN OXIDES

The just described reaction chains which contribute to the dissociation and re-formation of water vapor are not yet adequate since the formation and destruction of H, OH and HO_2 may depend on reactions with nitric oxide.

A rapid reaction [PHILLIPS and SCHIFF, 1962] such as

$$(a_{25}); \; H + NO_2 \rightarrow OH + NO + 30 \text{ kcal} \qquad (35a)$$

with a rate coefficient

$$a_{25} = 2 \times 10^{-12} \, T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \qquad (35b)$$

is not an important aeronomic process compared with another rapid reaction [TYLER, 1962]

$$(a_{26}); \; HO_2 + NO \rightarrow OH + NO_2 + 9 \text{ kcal} \qquad (36a)$$

No data are available on the rate coefficient. Assuming two extreme values

$$a_{26} = 3 \times 10^{-12} \, T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \qquad (36b)$$

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

$$a_{26} = 3 \times 10^{-12} \, T^{1/2} \, e^{-1250/T} \text{ cm}^3 \text{ sec}^{-1} \qquad (36c)$$

leading to about 10^{-11} cm^3 sec^{-1} at 500°K, it is possible to see that a leading role could be played by (36a) if $n(NO) > 10^8$ cm^{-3} in the stratosphere. Thus equation (20) must be replaced in the lower stratosphere by

$$\frac{n(HO_2)}{n(OH)} = \left\{\frac{a_1\ n(M)\ n(O_2)\ a_5\ n(O)}{a_1\ n(M)\ n(O_2) + a_2\ n(O_3)} + a_6\ n(O_3)\right\} \Big/ \left\{a_7\ n(O) + a_{26}\ n(NO)\right\} \tag{37}$$

which is an approximation of the more general equation

$$\frac{n(HO_2)}{n(OH)} = \left\{\frac{a_1\ n(M)\ n(O_2)\ a_5\ n(O)}{a_1\ n(M)\ n(O_2) + a_2\ n(O_3)} + a_6\ n(O_3)\right\} \Big/ \left\{J_{HO_2} + a_7\ n(O) + a_{17}\ n(OH) + a_{26}\ n(NO) + 2\ a_{27}\ n(HO_2)\right\} \tag{38}$$

where the various loss processes of HO_2 are considered, namely photodissociation, the reaction with OH and the production of hydrogen peroxide.

The photodissociation process (6)

$$H_2O_2 + h\nu \rightarrow OH + OH \tag{39}$$

does not seem to be an important mechanism even if the photodissociation coefficient for zero optical depth is not less than 10^{-4} sec^{-1}. In the stratosphere it reaches less than 5×10^{-6} sec^{-1} at 20 km. Among the several loss processes the reaction with a hydroxyl radical

$$(a_{30});\ OH + H_2O_2 \rightarrow H_2O + HO_2 + 30\ kcal \tag{40}$$

seems to be the most important mechanism since [GRENIER, 1968].

$$a_{30} = 4 \times 10^{-13}\ T^{1/2}\ e^{-600/T}\ cm^3\ sec^{-1}. \tag{41}$$

If nitrogen oxides are involved [NICOLET, 1965], hydrogen peroxide decomposes according to overall reactions which may come, for example, from

$$(a_{32})\ ;\ NO + H_2O_2 \rightarrow HNO_2 + OH + 11 \text{ kcal} \tag{42}$$

$$(a_{33})\ ;\ NO_2 + H_2O_2 \rightarrow HNO_3 + OH + 4 \text{ kcal} \tag{43}$$

for which the rate coefficients are not known. It is clear that of the various reactions which the oxides of nitrogen can undergo with hydrogen peroxide those which may give nitrous acid and nitric acid respectively must be considered. In order to reach about 10^{-12} cm^3 sec^{-1} at 30 km, a rate coefficient

$$a_{32} = a_{33} = 5 \times 10^{-12}\ T^{1/2}\ e^{-1000/T}\ \text{cm}^3\ \text{sec}^{-1} \tag{44}$$

with an activation energy of not more than 2 kcal is required. With such a value, NO and NO_2 concentrations greater than 10^8 cm^{-3} lead to loss coefficients of H_2O_2 greater than the photodissociation coefficient. It seems possible, therefore, that nitrogen oxides can affect the concentration of H_2O_2 in the stratosphere and that the ratio $n(OH)/n(HO_2)$ depends on the action of nitric oxide.

Hence, the following equation must be used

$$\frac{dn(H_2O_2)}{dt} + n(H_2O_2)\left[J_{H_2O_2} + a_{32}\ n(NO) + a_{33}\ n(NO_2)\right] = a_{27}\ n^2(HO_2) \tag{45}$$

in order to determine the behavior of hydrogen peroxide in the stratosphere and mesosphere.

The fact that nitric acid has been recently observed in the stratosphere [MURCRAY et al, 1968; 1969] is an indication that the nitrogen oxides play a role in a hydrogen-oxygen atmosphere. This shows that the introduction of nitrogen oxides decreases the concentration of hydroperoxyl radicals and hydrogen peroxide produced in an ozone-atomic oxygen atmosphere. In place of the simple scheme presented in Figure 9 it is necessary to consider the whole system (Figure 11) not only with the dissociation of H_2O into OH and H and the oxidation of H_2O leading to two OH radicals, but also with respect to the re-formation of water vapor by reaction between OH and HO_2 with concentrations (Figure 12) depending on reactions of HO_2 and H_2O_2 with nitrogen oxides.

VII. MOLECULAR HYDROGEN

The principal sink of molecular hydrogen in the stratosphere and mesosphere is (7) which leads to the following values of the oxidation coefficient for an overhead sun:

Altitude(km)	20	30	40	50	60	70
(sec^{-1})	2.5×10^{-10}	4.4×10^{-9}	4.4×10^{-8}	7.9×10^{-8}	3.3×10^{-8}	1.2×10^{-8}

The most important source of molecular hydrogen [BATES and NICOLET, 1965]

$$(a_{23})\ ;\ H + HO_2 \rightarrow H_2 + O_2 + 57\ \text{kcal} \qquad (46a)$$

with a rate coefficient which can be given by

$$a_{23} = 5 \times 10^{-12}\ T^{1/2}\ e^{-1000/T} \qquad (46b)$$

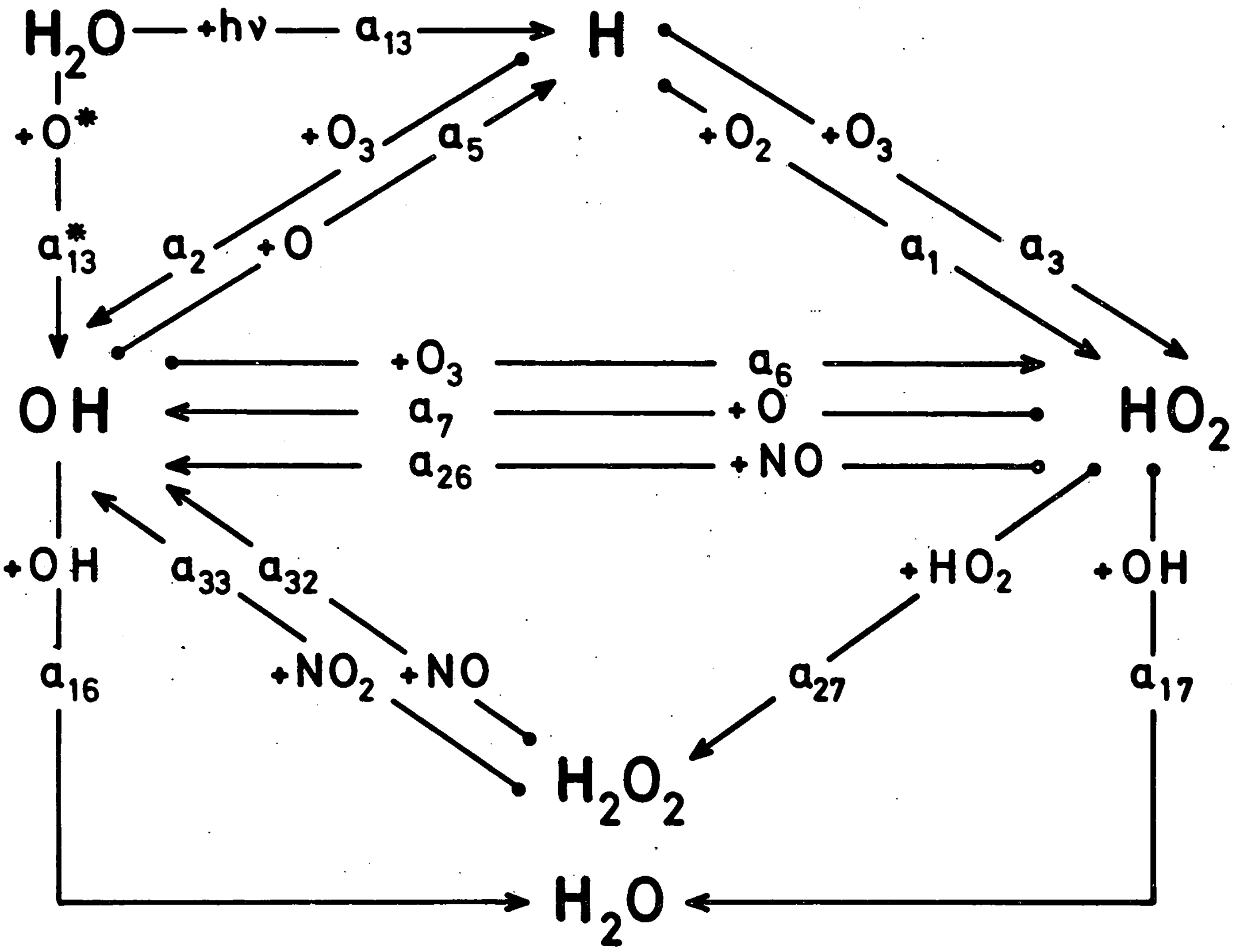

FIGURE 11

Fundamental H_2O reaction scheme. Initiating and terminating reactions depend on the production and destruction of hydroxyl radicals. Nitrogen oxides are involved and nitric acid must be formed.

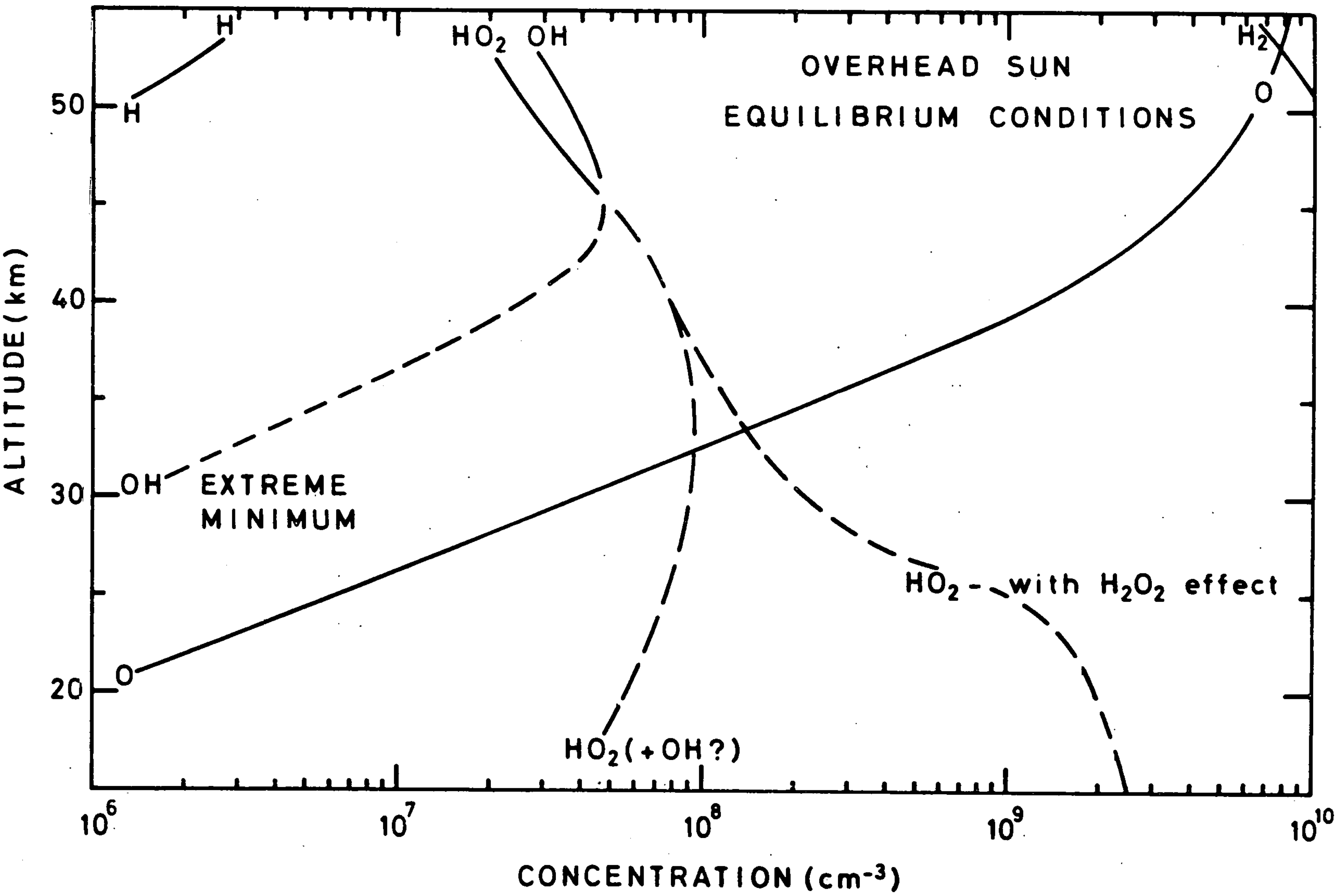

FIGURE 12

Concentrations of hydroxyl and hydroperoxyl radicals depending on reactions with nitrogen oxides. Extreme minimum of OH and extreme maximum of HO_2 without nitrogen oxides effect on HO_2 and H_2O_2, respectively.

leads to an important production of hydrogen molecules in the upper mesosphere (cf Table IV for H and HO_2 concentrations). The production is

Altitude (km)	50	60	70	75	80	85
($cm^{-3}\ sec^{-1}$)	7×10^1	8×10^1	4.5×10^1	3×10^2	3.5×10^3	4×10^1

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 (7) converts it into atomic hydrogen and hydroxyl radicals. It also flows upwards into the thermosphere. However, the exact distribution depends on the eddy diffusion coefficient which is introduced into the continuity equation

$$\frac{\partial n(H_2)}{\partial t} + \frac{\partial [n(H_2)\ w]}{\partial z} = a_{23}\ n(H)\ n(OH) \qquad (47)$$

where w is the eddy diffusion velocity given by (15).

A reliable estimate of the concentration of molecular hydrogen could be made only with appropriate values of the eddy diffusion coefficient which unfortunately are not known for the whole mesosphere, from the stratopause to the mesopause.

TABLE IV

Comparison of the Daytime Concentrations of O_3, OH and HO_2 for Concentrations of Atomic Oxygen and Hydrogen Depending on Mixing Conditions in the Lower Thermosphere. At and Below 70 km, Photochemical Conditions

Altitude (km)	n(O) (cm^{-3})	n(O_3) (cm^{-3})	n(H) (cm^{-3})	n(OH) (cm^{-3})	n(HO_2) (cm^{-3})
100	$3.2x10^{11}$	$1.6x10^{6}$	$3.5x10^{7}$	$1.7x10^{2}$	6.5
95	$3.3x10^{11}$	$1.3x10^{7}$	$8.7x10^{7}$	$3.2x10^{3}$	$1.4x10^{2}$
90	$3.0x10^{11}$	$1.1x10^{8}$	$2.3x10^{8}$	$7.0x10^{4}$	$4.5x10^{3}$
85	$3.0x10^{10}$	$1.0x10^{8}$	$6.9x10^{8}$	$2.0x10^{6}$	$5.3x10^{5}$
80	$1.4x10^{10}$	$1.4x10^{8}$	$8.6x10^{8}$	$2.2x10^{7}$	$1.7x10^{7}$
75	$3.8x10^{9}$	$3.2x10^{8}$	$5.1x10^{7}$	$1.8x10^{7}$	$1.3x10^{7}$
70	$4.1x10^{9}$	$1.0x10^{9}$	$1.0x10^{7}$	$9.5x10^{6}$	$7.0x10^{6}$
65	$5.1x10^{9}$	$3.2x10^{9}$	$6.0x10^{6}$	$1.3x10^{7}$	$8.7x10^{6}$
60	$6.6x10^{9}$	$1.0x10^{10}$	$4.4x10^{6}$	$1.9x10^{7}$	$1.2x10^{7}$
55	$8.5x10^{9}$	$3.2x10^{10}$	$3.3x10^{6}$	$2.8x10^{7}$	$1.6x10^{7}$
50	$6.5x10^{9}$	$1.0x10^{11}$	$1.2x10^{6}$	$4.4x10^{7}$	$2.8x10^{7}$

VIII. OZONE AND ATOMIC OXYGEN IN A HYDROGEN-OXYGEN ATMOSPHERE

In the stratosphere there is no important difference between a pure oxygen atmosphere and a hydrogen-oxygen atmosphere. This happens when the effect of hydrogen peroxide is not considered as a constituent playing an important aeronomic role and when the effect of nitric oxide and of nitrogen peroxide is important. Concentrations of NO_2 and NO greater than 10^8 cm^{-3} lead to a sufficient destruction of H_2O_2.

The conventional stratospheric equation

$$\frac{dn(O_3)}{dt} + 2n^2(O_3) \frac{J_3 k_3}{k_2\, n(M)\, n(O_2)} = 2n(O_2)\, J_2 \tag{48}$$

where the coefficients correspond to the following processes:

(J_2) ; $O_2 + h\nu\ (\lambda < 2420\ A) \rightarrow O + O$ (49a)

(J_3); $O_3 + h\nu \rightarrow O_2 + O$ (49b)

(k_2) ; $O + O_2 + M \rightarrow O_3 + M$ (49c)

(k_3) ; $O + O_3 \rightarrow 2\,O_2$ (49d)

must be replaced by

$$\frac{dn(O_3)}{dt} + 2n^2(O_3) \frac{J_3 k_3}{k_2\, n(M)\, n(O_2)} + n(O_3)\, a_2\, n(H)$$

$$n(O_3) \left\{ \left[\frac{a_5 J_3}{k_2\, n(M)\, n(O_2)} + a_6 \right] n(OH) + \left[\frac{a_7 J_3}{k_2\, n(M)\, n(O_2)} + a_{6c} \right] n(HO_2) \right\}$$

$$= 2n(O_2)\, J_2 \tag{50}$$

in which the effect of H, OH and HO_2 reactions is represented by the symbol a from reactions (22), (25), (26) and (27).

If (50) is compared with (46), it is clear that the effect of hydrogen compounds is equivalent to an increase of the photodissociation coefficient J_3. In other words, the ozone photodissociation is increased by additional destruction processes of oxygen atoms [BATES and NICOLET, 1950; HAMPSON, 1965; HUNT, 1966; HESSTVEDT, 1968; CRUTZEN, 1969] so that the equivalent O_3 photodissociation coefficient J_{3A} is written

$$J_{3A} = J_3 \, [1 + A] \tag{51}$$

where A is given by

$$A = \frac{a_2 \, n(H) \, k_2 \, n(M) \, n(O_2)}{2 \, J_3 \, k_3 \, n(O)} + a_5 \, n(OH) \left[1 + \frac{a_6}{a_5} \, \frac{k_2 \, n(M) \, n(O_2)}{J_3} \right]$$

$$+ a_7 \, n(HO_2) \left[1 + \frac{a_{6c}}{a_5} \, \frac{k_2 \, n(M) \, n(O_2)}{J_3} \right] \tag{52}$$

The conventional equation for equilibrium conditions in the stratosphere is replaced by, using (50) and (51),

$$n(O_3) = \left[\frac{k_2}{k_3} \, n(M) \, n^2(O_2) \, . \, \frac{J_2}{J_3 \, (1 + A)} \right]^{1/2} \tag{53}$$

The correction term $[1 + A]^{1/2}$ in the stratosphere where n(H) is negligible, a_{6c} very small, and $a_7 \simeq a_5$, can be written

$$[1 + A]^{1/2} = \left[1 + \frac{a_7 \, \{ n(HO_2) + n(OH) \}}{2 k_3 \, n(O_3)} \right] \simeq 1.5 \quad . \tag{54}$$

An illustration of such an effect is given in Figure 13 which shows that below 35 km the vertical distribution of the ozone concentration corresponds to a departure from photochemical conditions. Transport processes are responsible for the determination of the vertical

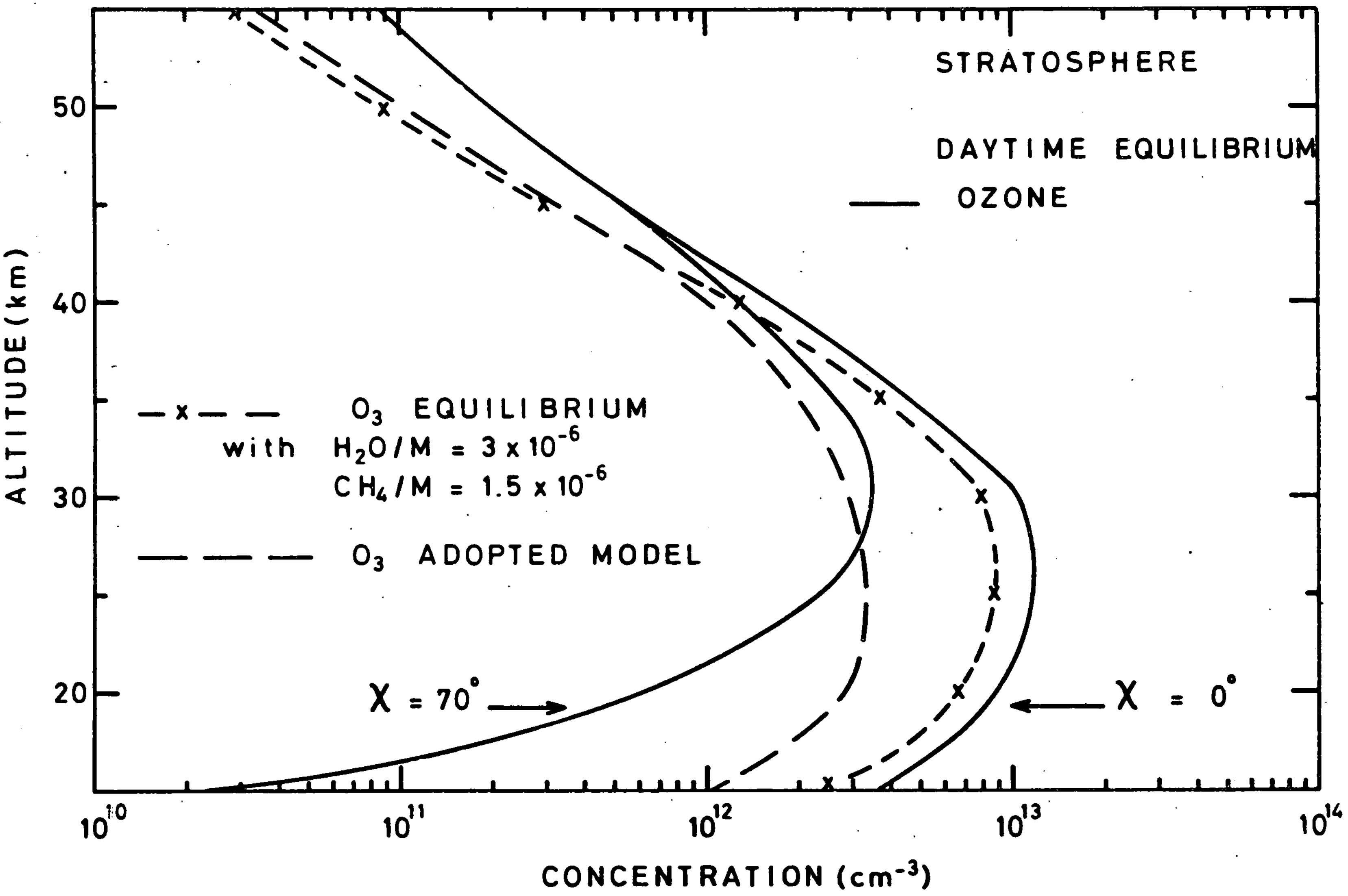

FIGURE 13

Vertical distribution of the ozone concentration in the stratosphere for equilibrium conditions without the effect of hydrogen constituents ($\chi = 0^{\circ}$ and 70°) and with the effect of OH and HO_2 reactions; and the adopted model for calculation.

distribution. The equivalent value of the mixing ratio $n(H_2O)/n(M)$ which is adopted is 6.5×10^{-6}. Such a ratio has a small effect on the ozone concentration in the stratosphere (cf 54), and it seems that almost impossibly high mixing ratios (5×10^{-5}, 10^{-4}) would be required in order to affect in a very sensitive 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

$$[1 + A]^{1/2} = \left[1 + \frac{a_2\, n(H)\, k_2\, n(M)\, n(O_2)/J_3 + a_5\, n(OH) + a_7\, n(HO_2)}{2k_3\, n(O_3)}\right]^{1/2} \tag{55}$$

increases from 1.5 at the stratopause to about 100 at the mesopause for the calculated values of H, OH and HO_2 concentrations as indicated in Figure 14. There is a considerable decrease of the atomic oxygen concentration in the mesosphere and consequently a parallel decrease of the ozone concentration. Figure 15 illustrates the difference between an oxygen mesosphere and a hydrogen-oxygen mesosphere.

In the thermosphere where atomic hydrogen is the most important hydrogen constituent, $n(H)/n(OH) > 1$ and $n(H)/n(HO_2) > 1$, its vertical distribution may correspond to a mixing distribution. [KOCKARTS and NICOLET, 1962]. At 100 km a concentration of the order of 3.5×10^{7} cm^{-3} which leads to an escape rate of 10^{8} atoms cm^{-2} sec^{-1} corresponds to the equivalent mixing ratio $n(H_2O)/n(M) = 6.5 \times 10^{-6}$, i.e. the adopted value for the reaction of $O(^1D)$ atoms. It has been shown [KOCKARTS and NICOLET, 1962] that a molecular diffusion flow at the 100 km level

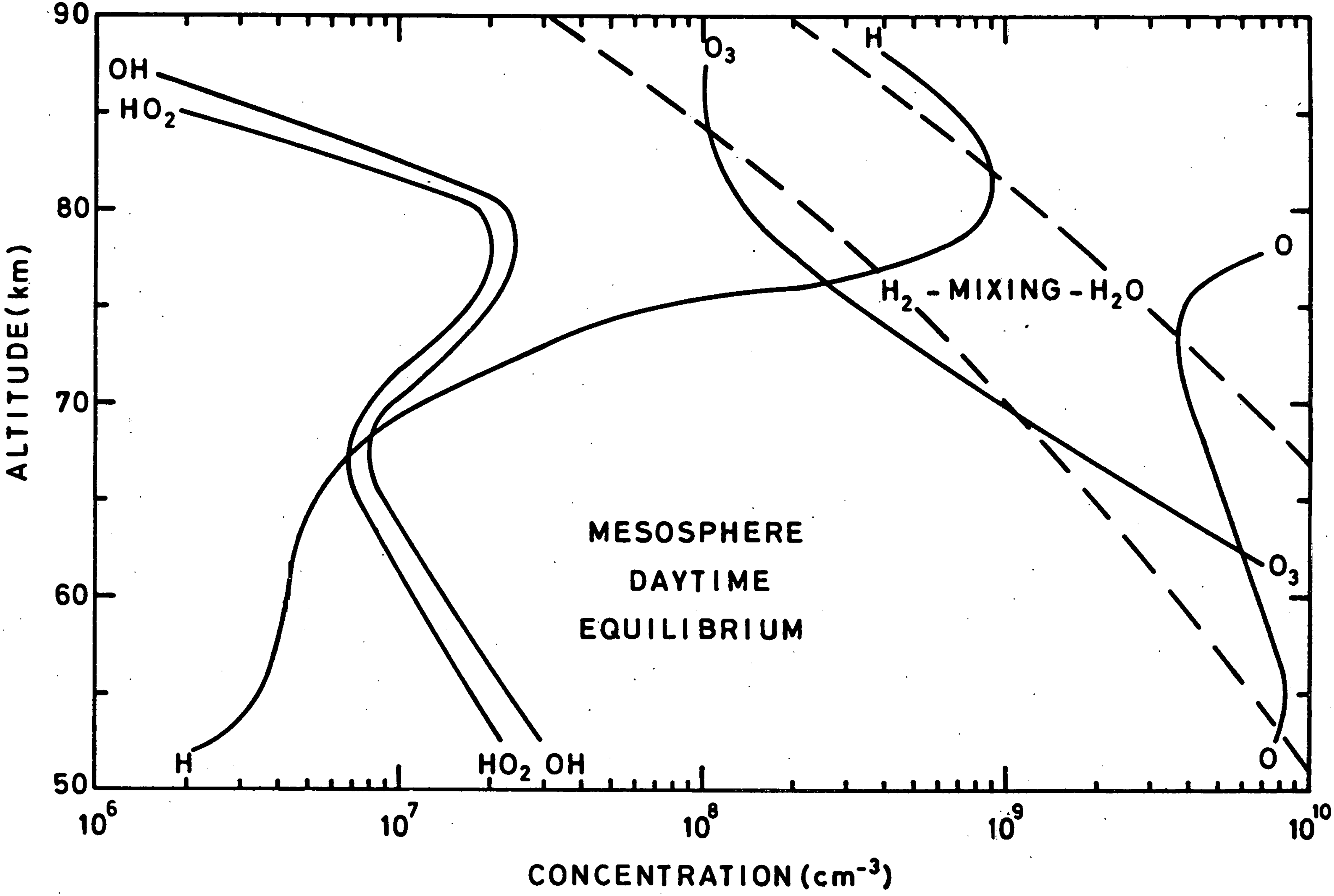

FIGURE 14

Example of the vertical distribution of the H, OH and HO$_2$ concentrations which are in photoequilibrium in the mesosphere. The mesopause corresponds to a transition region.

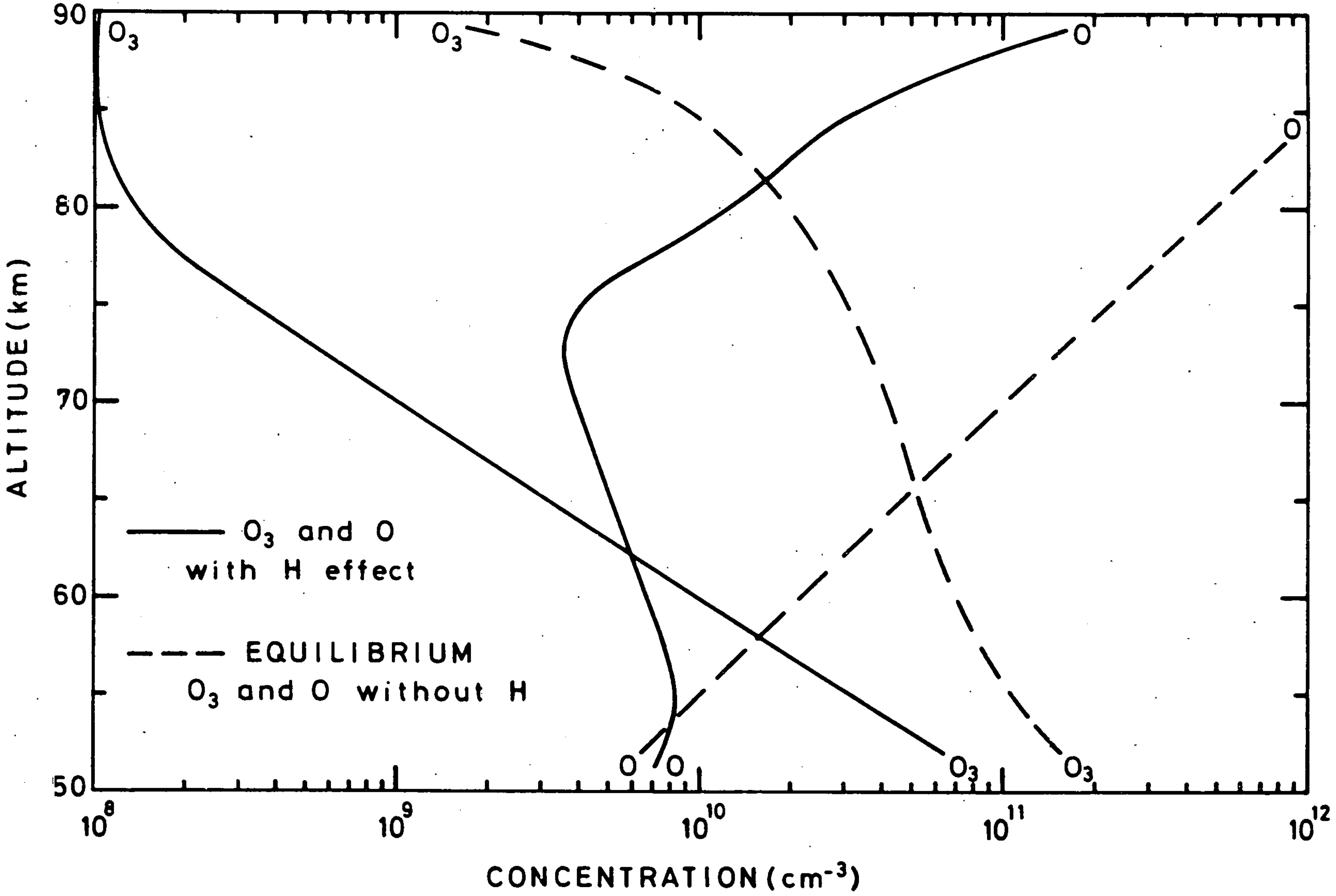

FIGURE 15

Differences in the O and O_3 concentrations for a pure oxygen-nitrogen atmosphere and a hydrogen-oxygen atmosphere. Decrease of the ozone concentration due to hydrogen from about 1.5 at 50 km up to a factor of 100 at the mesopause.

of $F_D(H) = 2.5 \times 10^7\ cm^{-2}\ sec^{-1}$ corresponds to an atomic hydrogen concentration of $10^7 cm^{-3}$; with $n(H)_{100\ km} = 3.5 \times 10^7\ cm^{-3}$, $F_D(H) \simeq 10^8\ cm^{-2}\ sec^{-1}$. Under mixing conditions, molecular diffusion flow of water vapor $F_D(H_2O) = 5 \times 10^7\ cm^{-2}\ sec^{-1}$ requires a mixing ratio of the order 6×10^{-6}, while the molecular diffusion flow of methane with the mixing ratio 1.5×10^{-6} is $F_D(CH_4) = 7 \times 10^6\ cm^{-2}\ sec^{-1}$ which is about 50% of the molecular diffusion flow of atomic hydrogen.

It may be easily seen from Table IV where the concentrations of atomic oxygen in the thermosphere ($\geq$ 85 km) are fixed according to arbitrary eddy diffusion conditions and the concentrations of atomic hydrogen also in the thermosphere ($\geq$ 85 km) follow a mixing distribution calibrated at 100 km in order to give $n(H) = 3$ to $4 \times 10^7\ cm^{-3}$, that ozone is still important while the hydroxyl and hydroperoxyl radicals concentrations are very small. Photochemical or chemical equilibrium conditions in the lower thermosphere between O and O_3 are given by the ratio

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

since $J_3 = 10^{-2}\ sec^{-1}$ and $a_2\ n(H)$ is the same order. Thus the vertical distribution of the ozone concentration in the thermosphere depends on the vertical distribution of the atomic oxygen concentration which may vary. Furthermore, there is an increase of the ozone concentration after sunset when $J_3 = 0$ if there is no simultaneous decrease of the atomic oxygen concentration. Dynamic effects acting on the vertical distribution of atomic oxygen modify the ozone distribution in the lower thermosphere and can explain the molecular oxygen emission in the airglow [EVANS and LLEWELLYN, 1970] .

Below the mesopause, 85 to 80 km, the aeronomic conditions are such that they correspond to a transition region, and all concentrations in this altitude range are intermediate values between those resulting from mixing and from photochemical equilibrium. Such an aspect is clearly seen in Figure 14 where there is a discontinuity in the curves around 80 km. The discontinuity as it is shown in that figure must be considered only as an illustration of the extreme variability of aeronomic conditions below the mesopause. In other words, it must be stressed that any theoretical analysis in this part of the higher mesosphere and lower thermosphere is idealized and differs from the true atmosphere in that a discontinuity occurs which varies between day and night and with latitude and season depending on atomic oxygen subject to dynamic processes.

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