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# STABILITY OF THE MARTIAN ATMOSPHERE

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## Abstract

A detailed chemical dynamic model is presented for a moist Martian atmosphere. Recombination of $CO_2$ is catalyzed by trace amount of $H_2O$. The abundances of CO and $O_2$ should vary in response to changes in atmospheric $H_2O$ and atmospheric mixing.

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Carbon dioxide is the major gaseous component in the atmospheres of both Mars and Venus and it is difficult to understand its apparent stability. The gas is readily dissociated by sunlight at wavelengths less than 2000Å. However, recombination of $CO_2$ by the elementary reaction

$$CO + O + M \rightarrow CO_2 + M \tag{1}$$

proceeds at a rate which is negligibly slow (1) compared with the competing reaction

$$O + O + M \rightarrow O_2 + M \tag{2}$$

It would appear therefore that the atmospheres of Mars and Venus should contain large amounts of $O_2$ and CO, and yet both atmospheres are remarkably deficient in dissociation products such as CO, $O_2$, $O_3$ and O.

We shall argue here that recombination occurs predominantly between CO and O and proceeds catalytically by the reaction sequence

$$H + O_2 + M \rightarrow HO_2 + M \tag{3}$$

$$O + HO_2 \rightarrow OH + O_2 \tag{4}$$

$$CO + OH \rightarrow CO_2 + H \quad . \tag{5}$$

Photolysis of $H_2O$ provides the source of hydrogen radicals (2). This sequence readily accounts for removal of oxygen atoms below about 25 km. At higher altitudes the $HO_2$ concentration is vanishingly small, a consequence of the strong dependence on altitude of the three body reaction (3). The alternate scheme

$$H + O_3 \rightarrow OH + O_2 \tag{6}$$

followed by (5) plays some role at higher altitudes where ozone is produced mainly by

$$O + O_2 + M \rightarrow O_3 + M \tag{7}$$

and removed by photolysis in the Hartley continuum

$$h\nu + O_3 \rightarrow O + O_2 \quad . \tag{8}$$

A viable photochemical model must also account for a chemical balance in $O_2$. Molecular oxygen is formed by (2) and by

$$O + OH \rightarrow O_2 + H \tag{9}$$

Both reactions provide large potential sources of $O_2$ above 20 km. Molecular oxygen diffuses downward and is removed by photolysis in the Herzberg continuum

$$h\nu + O_2 \rightarrow O + O \quad , \tag{10}$$

followed by reactions (3) - (5), with some additional removal associated with the reaction sequence (3)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

$$h\nu + H_2O_2 \rightarrow 2OH \tag{12}$$

followed by reaction (3). However, the bulk of the recombination is due to reactions (3) - (5). This is a consequence of rapid downward transport of oxygen atoms which suppresses the formation of $O_2$.

An alternate scheme (2,4) for recombination of CO and $O_2$ involves reaction (3) followed by

$$CO + HO_2 \rightarrow CO_2 + OH \tag{13}$$

and reaction (5). We shall argue that reaction (13) is too slow to play a role for Mars.

The importance of $H_2O$ in the Martian atmosphere was emphasized earlier in another context (5). Recombination of $O_2^+$ in the Martian exosphere leads to production of energetic oxygen atoms and a significant number of O atoms escapes to interplanetary space. The estimated escape rate for O is approximately equal to half the observed escape rate for H. The H atoms are supplied to the upper atmosphere by upward diffusion of $H_2$ formed as a by-product of $H_2O$ chemistry in the near surface region. The primary source of $H_2$ is the reaction

$$H + HO_2 \rightarrow H_2 + O_2 \qquad (14)$$

and the net production of $H_2$ is determined by the magnitude of the O atom escape rate. It was argued that the relative concentrations of CO and $O_2$ in the lower atmosphere would be moderated as a result of oxygen escape so as to supply the required upward flux of $H_2$. Escape of oxygen acts therefore to determine the magnitude of the quantity

$$I = \int_0^\infty k_{14} [H][HO_2]\, dz \qquad (15)$$

where $[H]$ and $[HO_2]$ are number densities of H and $HO_2$ at height z and $k_{14}$ is the rate constant for reaction (14). Using the analyses by Hunten and McElroy (2) and McElroy (5) we estimate $I = 3.5 \times 10^8$ cm$^{-2}$ sec$^{-1}$ with a probable uncertainty of about a factor of 2. An acceptable chemical model for Mars is constrained therefore to provide the appropriate value for I.(6)

Detailed numerical studies of Martian photochemistry are simplified by a number of factors. First, $O_2$ and CO may be assumed to be in diffusive equilibrium over an extensive altitude regime. The relevant photochemical time constants are long compared to any conceivable transport times. We may therefore assume that the abundances of CO and $O_2$ are known and adopt the observed mixing ratios of $8 \times 10^{-4}$ (7) and $1.3 \times 10^{-3}$ (18) respectively. Secondly, the concentration of odd hydrogen, $[H] + [HO_2] + [OH]$, should also be well mixed in view of the relatively long time constants for radical removal. The principal paths for radical loss are (14) and

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (16)$$

The dominant radical below 25 km is $HO_2$. Atomic hydrogen dominates at higher altitudes and the mixing ratio of odd hydrogen, for given $O_2$ and CO, is specified by the conservation condition (15). With the model employed here we find a mixing ratio for odd hydrogen equal to $5.0 \times 10^{-10}$.

The detailed chemical model is summarized in Table 1. The important rate constants are moderately well known, with two exceptions. Reaction (11) is currently in some dispute. Clark (1), noted that extrapolation of high temperature data obtained by Baldwin et al. (9) implied a rate constant at Martian temperatures of order $10^{-30}$ $cm^3$ $sec^{-1}$. Davis (10) determined an upper limit for the reaction at room temperature equal to $10^{-18}$ $cm^3$ $sec^{-1}$. On the other hand Westenberg and DeHaas (11) concluded that the rate constant at room temperature was fast, equal to approximately 0.06 times the rate constant for reaction (15). The choice of rate constant in Table 1, $k_{11} < 10^{-16}$ $cm^3$ $sec^{-1}$, reflects a careful study of the available data. We note for example that Westenberg and De Haas (11) did not allow for the fast reaction (16) as a loss mechanism for OH. On the basis of our current understanding of Mars it would be difficult to accept a value of $k_{12}$ much larger than the upper limit adopted here (12).

Some uncertainty is associated also with $k_{14}$. Kaufman (13) concluded that $k_{14}$ should exceed $3 \times 10^{-12}$ $cm^3$ $sec^{-1}$, reflects a recent analysis of the available data by McConnell (14). A smaller value for $k_{14}$ would imply somewhat larger mixing ratios for odd hydrogen and lower values for the eddy mixing coefficient near 30 km but should not significantly alter the general characteristics of the photochemical model. In particular, recombination of O and CO would continue to occur primarily by reactions (3) - (5), although photolysis of $H_2O_2$ would be relatively more important as a sink for $O_2$.

Concentrations of odd oxygen were obtained by numerical solution of the coupled diffusion - continuity equations. Odd oxygen is produced by photolysis of $CO_2$ and $O_2$. We used recent data by Widing et al. (15) to compute dissociation rates. Their fluxes are somewhat lower than values employed in earlier calculations (16) and photolysis rates are similarly reduced. The net production of O in the present model is equal to $1.8 \times 10^{12}$ cm$^{-2}$ sec$^{-1}$. Loss of odd oxygen is primarily by (5), with some contribution from (9) and (2). Results for the principal constituents are shown in Figure 1. This model corresponds to a vertical eddy diffusion coefficient of $1.5 \times 10^{8}$ cm$^{2}$ sec$^{-1}$ and is most sensitive to the diffusion coefficient in the vicinity of 30 km. The magnitude of the diffusion coefficient derived here is similar to values discussed by Gierasch and Goody (17) in their study of energy transfer in the Martian troposphere. According to calculations by McElroy and McConnell (16) somewhat larger eddy coefficients, $\sim 10^{9}$ cm$^{2}$ sec$^{-1}$, are required at higher elevations (above 60 km) in order to account for upper atmospheric data on O and CO.

The relative importance of various source and sink terms is illustrated in Figure 2. The quantities plotted here are rates of various reactions, integrated from the Martian surface to height z (km). The integrated rate of $CO_2$ photolysis is also shown. The difference between this rate and the total recombination rate reflects the contribution of flow to the local atomic oxygen production rate. Evidently CO-O recombination occurs mainly below 25 km, and the reaction sequence (3) - (5) is the dominant path for recombination. Formation of $O_2$ occurs in a restricted altitude regime, between 25 km and 30 km, and reaction (9) dominates. The rate of reaction (16) obtained from Figure 1 implies an average rate for photolysis of $H_2O$ equal to $2.7 \times 10^9$ $cm^{-2}$ $sec^{-1}$, in agreement with earlier estimates (2) of the mean photolysis rate based on observed $H_2O$ concentrations (18). The model predicts an $O_3$ abundance of $1.4 \times 10^{-4}$ cm atm., in satisfactory agreement with limits set by the ultraviolet experiments on Mariners 6, 7, and 9 (19). Ozone is normally a minor source of ultraviolet opacity in the Martian atmosphere although occasionally strong absorption is detected. High ozone concentrations are apparently correlated with unusually cold atmospheric conditions, (19), and may be a natural consequence of the chemical model discussed here. One would expect lower concentrations of $H_2O$ and consequently OH, $HO_2$ and H in colder regions of the Martian atmosphere. Wet chemistry is less effective and odd oxygen concentrations should be consequently higher. This matter will be discussed in detail elsewhere.

The response of the Martian atmosphere to a change in the concentration of $H_2O$ is of considerable interest. For modest changes, the atmosphere readily adjusts to a new equilibrium state with a different mixing ratio of CO relative to $O_2$. To first order, the concentration of OH is proportional to the concentration of $H_2O$ and the concentrations of O, H, and $HO_2$ in the lower atmosphere remain constant. Only CO changes, and the change is inversely proportional to the change in $H_2O$. To a higher level of approximation, however, one must take account of consequent changes in the $O_2$ production and one finds necessarily some decrease (or increase) in $O_2$ associated with a decrease (or increase) in $H_2O$. By numerical experimentation we found that if the $H_2O$ concentration were arbitrarily reduced by a factor of 2, the CO concentration would increase by a similar factor and $O_2$ would decrease by about 50%, if the eddy mixing coefficient remained constant.

It is of interest to consider also the atmospheric response to a change in the eddy mixing coefficient near 30 km. A reduction (or increase) in the eddy mixing coefficient at 30 km leads to an increase (or decrease) in $O_2$ formation. The chemical equilibrium in the lower atmosphere is altered with a consequent increase (or decrease) in the abundance of CO and $O_2$. The mixing ratio of CO relative to $O_2$ remains relatively constant. The suggestion of a time variable $O_2$ concentration in the late stages of the recent planet-wide dust storm (8) may reflect in part a change in the dynamic state of the atmosphere, in part a change in atmospheric $H_2O$. It is difficult however, to draw more quantitative conclusions. A complete analysis should allow for heterogeneous chemistry on atmospheric dust and there are reasons to suspect that Martian dust may play some role in the chemistry of atmospheric oxygen (20).

Finally, we note the central importance in the present analysis of the conservation condition afforded by equation (15). The relative abundance of odd hydrogen, and the mixing ratio of odd hydrogen, are controlled by this relation in the present scheme. An increase (or decrease) in O escape, associated for example with increased (or decreased) solar activity, will result in an increase (or decrease) in atmospheric CO. The concentrations of OH in the lower atmosphere will change. For fixed $H_2O$, $HO_2$ will increase (or decrease) corresponding to an increase (or decrease) in O escape. The $H_2$ production and H escape will alter accordingly. The present model provides plausible justification for the observed relation between H and O escape and lends confidence to conclusions derived earlier (5) regarding the evolutionary history of Martian $H_2O$ (23).

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## Table 1

Relevant reactions with their rate constants. For 2 body reactions, units are $cm^3\ sec^{-1}$ and for 3 body reactions, units are $cm^6\ sec^{-1}$.

| | | |
|---|---|---|
| 1 | $CO + O + CO_2 \rightarrow CO_2 + CO_2$ | $k_1 = 2 \times 10^{-37}$ |
| 2 | $O + O + CO_2 \rightarrow O_2 + CO_2$ | $k_2 = 3 \times 10^{-33}(T/300)^{-2.9}$ |
| 3 | $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$ | $k_3 = 2 \times 10^{-31}(T/273)^{-1.3}$ |
| 4 | $O + HO_2 \rightarrow OH + O_2$ | $k_4 = 7 \times 10^{-11}$ |
| 5 | $CO + OH \rightarrow CO_2 + H$ | $k_5 = 9 \times 10^{-13}\exp(-500/T)$ |
| 6 | $H + O_3 \rightarrow OH + O_2$ | $k_6 = 2.6 \times 10^{-11}$ |
| 7 | $O + O_2 + CO_2 \rightarrow O_3 + CO_2$ | $k_7 = 1.4 \times 10^{-33}(T/300)^{-2.5}$ |
| 8 | $O_3 + h\nu \rightarrow O_2 + O$ | $J_8 = 4.2 \times 10^{-3}\ sec^{-1}$ |
| 9 | $O + OH \rightarrow O_2 + H$ | $k_9 = 5 \times 10^{-11}$ |
| 10 | $O_2 + h\nu \rightarrow O + O$ | $J_{10} = 5.8 \times 10^{-10}\ sec^{-1}$ |
| 11 | $CO + HO_2 \rightarrow CO_2 + OH$ | $k_{11} = < 10^{-16}$ |
| 12 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $k_{12} = 9.5 \times 10^{-12}$ |
| 13 | $H_2O_2 + h\nu \rightarrow OH + OH$ | $J_{13} = 5.2 \times 10^{-5}\ sec^{-1}$ |
| 14 | $H + HO_2 \rightarrow H_2 + O_2$ | $k_{14} = 1 \times 10^{-11}$ |
| 16 | $OH + HO_2 \rightarrow H_2O + O_2$ | $k_{16} = 2 \times 10^{-10}$ |

General References: Clark (1), Kaufman (13)

Rate Constants: $k_1$ (22, 23, 24), $k_3$(25), $k_4$(21), $k_7$(26), $k_{13}$(27), $k_{16}$(21).

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6. Molecular hydrogen is formed mainly by reaction (14) and removed by reactions with $O(^1D)$ and $CO_2^+$. A lower bound for I may be specified on the basis of the observed H escape. In addition we can derive an upper limit to the mixing ratio of $H_2$ if we assume that the bulk of the escaping H is provided by the $CO_2^+ + H_2$ reaction. This limit, $5 \times 10^{-5}$, can then be employed to estimate an upper bound for I, if the $O_3$ concentration is known. We find $8 \times 10^7 < I < 2 \times 10^{-7} \mathcal{N}$, where $\mathcal{N}$ defines the column density of $O_3$ ($cm^{-2}$) (19). With the present chemical model, $\mathcal{N} \simeq 3 \times 10^{15}$, close to the upper limit derived from Mariner 9 observations. Our choice for I reflects these considerations. A more elaborate calculation should consider the coupled flows of odd hydrogen and odd oxygen and the value of I would be specified accordingly. We were unable to find additional important sinks for $H_2$. For example, loss of $H_2$ by reaction with OH is less than $5 \times 10^7$ $cm^{-2}$ $sec^{-1}$ at Martian temperatures.

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12. The resulting destruction of $HO_2$ by CO if $k_{11}$ is much larger than $10^{-16}$ $cm^3$ $sec^{-1}$ would create great difficulties in maintaining physically reasonable odd hydrogen distributions. Furthermore, the large atomic oxygen densities needed to produce adequate recombination of O and CO would cause the $O_3$ concentration to go beyond acceptable limits.

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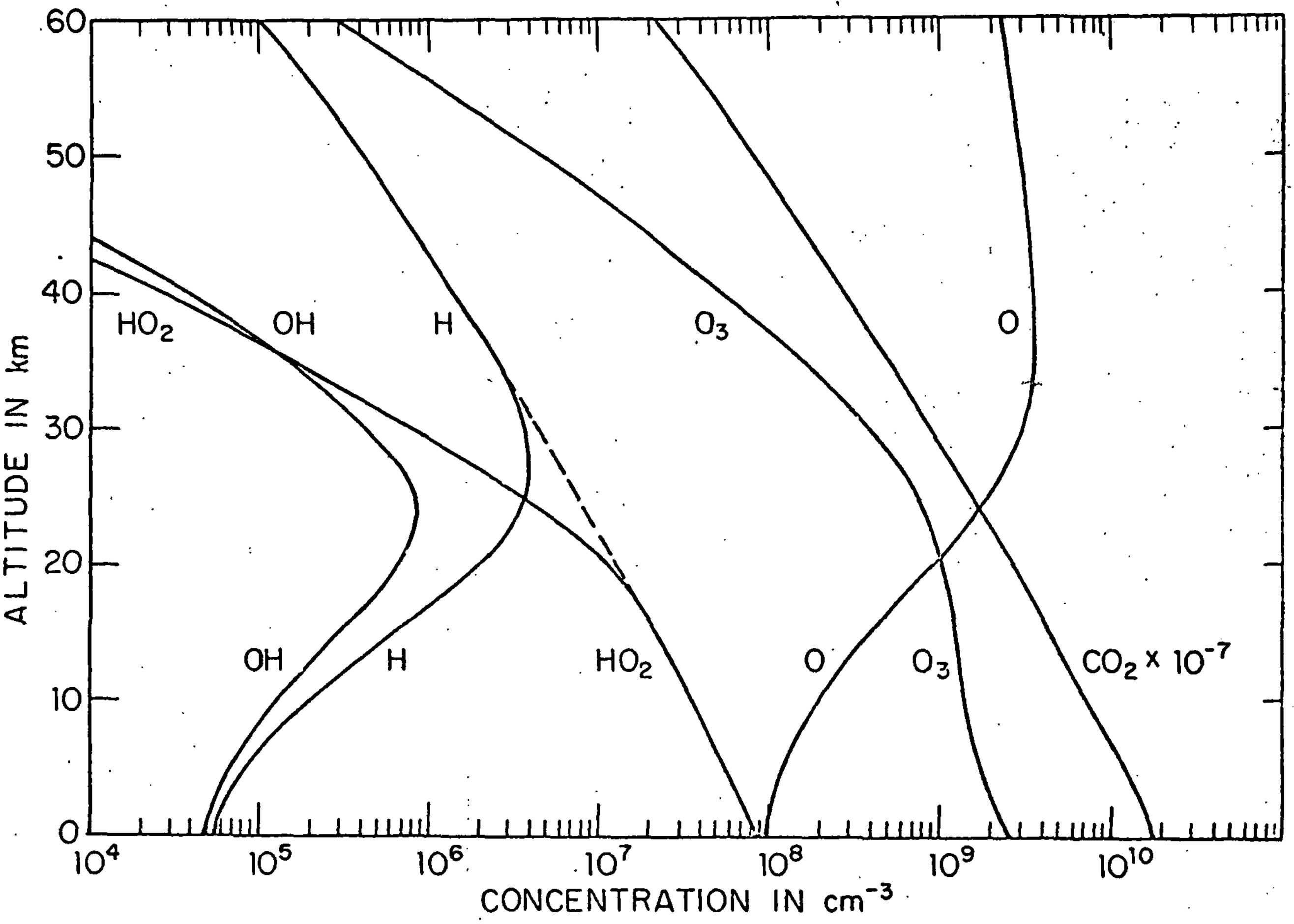
# Figures

Fig. 1 Concentration of principal constituents in the Martian Atmosphere. Surface temperature is 220°. Eddy diffusion coefficient is $1.5 \times 10^{8}$ $cm^{2}$ $sec^{-1}$. The curve for odd hydrogen, shown as a broken line between the portions labelled $HO_2$ and H, is plotted at $5 \times 10^{-10}$ times the $CO_2$ density. The $O_2$ and CO densities are respectively $1.3 \times 10^{-3}$ and $8 \times 10^{-4}$ times the $CO_2$ densities.

Fig. 2 Integrated reaction rates important in $CO_2$ and $O_2$ formation and loss. The curve labelled P(O) is the integrated photolysis rate for $CO_2$. The contribution from O + O + M is only $2.3 \times 10^{9}$ $cm^{2}$ $sec^{-1}$ and not shown.


ALTITUDE IN km
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10
20
30
40
50
60
CONCENTRATION IN $cm^{-3}$
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$10^5$
$10^6$
$10^7$
$10^8$
$10^9$
$10^{10}$
$HO_2$
OH
H
$O_3$
O
OH
H
$HO_2$
O
$O_3$
$CO_2 \times 10^{-7}$

**Figure 1**

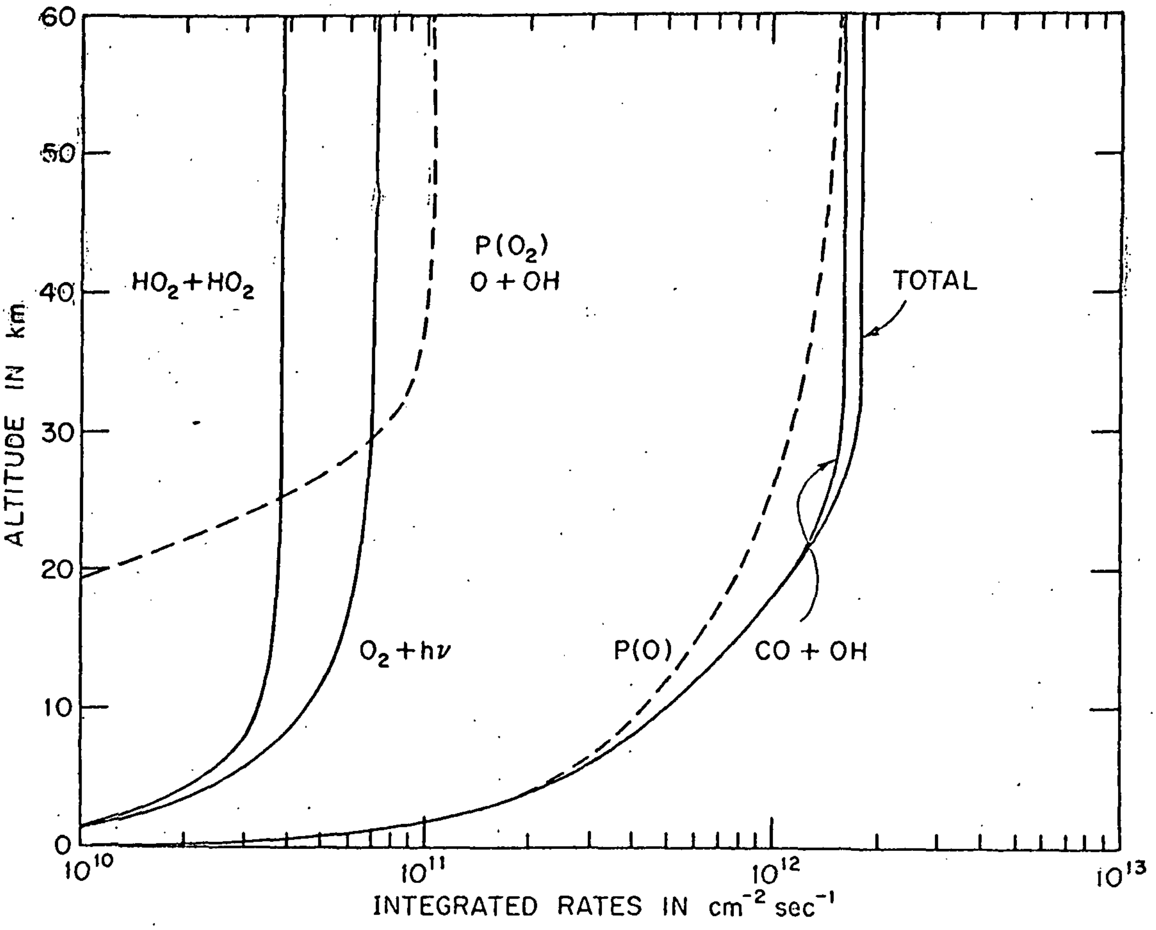
ALTITUDE IN km
0
10
20
30
40
50
60
INTEGRATED RATES IN $cm^{-2}$ $sec^{-1}$
$10^{10}$
$10^{11}$
$10^{12}$
$10^{13}$
$HO_2+HO_2$
$P(O_2)$
$O+OH$
$O_2+h\nu$
P(O)
CO + OH
TOTAL

Figure 2