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EVOLUTION OF THE ATMOSPHERE OF VENUS

The investigation focused on the influence that stratospheric chemistry may have on the evolution of the planet. Currently there are two competing theories for the escape of hydrogen from the Venusian atmosphere. Kumar et al. (1981) argued that the abundance of H_2 in the bulk atmosphere is $\sim$ 10 ppm. The escape of H is driven by the reaction

$$O^+ + H \rightarrow OH^* + H^*$$

where the hot hydrogen atom H^* has enough energy for escape. In the Kumar et al. model, the escape rate of hydrogen is of order 1×10^8 atoms $cm^{-2}s^{-1}$.

The other theory is due to McElroy (1981). This model assumes a lower concentration of H_2 in the atmosphere. The escaping atoms are produced by

$$O^* + H \rightarrow O + H^*$$

where O^*, the hot O atom is produced in

$$O_2^+ + e \rightarrow O^* + O^* \quad .$$

This theory predicts an escape rate of H of order 10^7 atoms $cm^{-2}s^{-1}$.

The chemistry in the stratosphere is capable of distinguishing these theories. H_2 is a important component in the neutral chemistry, via the crucial reaction

$$Cl + H_2 \rightarrow HCl + H \quad .$$

The modeling of the stratosphere has recently been completed, and the results are being prepared for publication in the *Journal of Geophysical Research*.

Manuscript in preparation:

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Photochemistry of the Stratosphere of Venus

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Abstract

The photochemistry of the stratosphere of Venus has been modeled using an updated and expanded chemical scheme, and the results of recent laboratory studies. Our model satisfactorily accounts for the observations of CO, O_2, $O_2(^1\ )$ and SO_2 in the stratosphere. Oxygen, derived from CO_2 photolysis, is primarily consumed by CO_2 recombination and oxidation of SO_2 to H_2SO_4. Photolysis of HCl in the upper stratosphere provides a major source of odd hydrogen radicals, essential for the catalytic oxidation of CO. Oxidation of SO_2 by O occurs in the lower stratosphere, with the O-O bond broken by $S + O_2$ and $SO + HO_2$. The sensitivity of stratospheric chemistry to ambient H_2 abundance has been studied and our model prefers the high value (~ 10 ppm) recently inferred from the Pioneer Venus ionospheric measurements. The importance of the photochemical production of S_2O, $(SO)_2$, S_2, $H_2S_2O_2$ and $H_2S_2O_3$ is speculated. Our modeling reveals a number of intriguing similarities, previously unsuspected, between the chemistry of the stratospheres of Venus and the Earth, and these results are briefly presented and discussed.

1. Introduction

The atmosphere of Venus is composed primarily of CO_2. Small concentrations of chemically active species such as CO, H_2O, HCl, $O_2(^1\ )$ and SO_2 have been detected in the stratosphere. The presence of H_2 in the bulk atmosphere has been inferred from ionospheric measurements. The current status regarding the abundance and distribution of the important chemical species in the stratosphere is summarized in Table 1. The purpose of this paper is to propose and examine a range of photochemical models that can satisfy the observational constraints, and at the same time are consistent with current experiments in chemical kinetics, some of which have recently been performed at the authors' institution. Unfortunately, neither the observations nor the kinetics can be considered complete and definitive, and this paper can only aspire to provide some motivation and useful guidelines for further work in both areas.

The stratosphere of Venus above the cloud tops (- 60 km) is the region where the bulk of solar ultraviolet radiation is absorbed. Photolysis of CO_2 occurs readily by absorption of photons shortward of 2040Å (Shemansky, 1972),

$$CO_2 + h \qquad CO + O \, . \tag{R1}$$

The recombination reaction,

$$CO + O + M \qquad CO_2 + M \tag{R14}$$

is, however, spin-forbidden, and a major loss of atomic oxygen is the formation of O_2 via:

$$O + O + M \quad O_2 + M \qquad (R17)\ ,$$

$$O + Cl \quad Cl + O_2 \qquad (R44)\ ,$$

$$O + OH \quad O_2 + H \qquad (R28)\ .$$

One would expect, on the basis of simple photochemical arguments, that CO and O_2 should be abundant and that the ratio $CO{:}O_2$ would be about 2:1. The observed mixing ratio of CO at the cloud top is 4.5×10^{-5} (Connes et al., 1968). The upper limit for O_2 is 1×10^{-6} (Traub and Carleton, 1974). A successful chemical model must account for the deficiency of CO in the upper atmosphere, and the extreme scarcity of O_2 relative to CO.

Early photochemical models have concentrated on the recombination of CO_2 mediated by catalytic cycles involving ClO_x (Cl, ClO, ClOO, Cl_2) (Prinn, 1971) and HO_x (H, OH, HO_2, H_2O_2) radicals (McElroy et al., 1973; Sze and McElroy, 1974), derived from photolysis of HCl (Connes et al., 1967; McElroy, 1970). Prinn (1971) proposed the scheme:

$$\begin{array}{ll} 1/2\ (Cl + O_2 + M & ClOO + M) \\ 1/2\ (ClOO + CO & CO_2 + ClO) \qquad (I) \\ 1/2\ (ClO + CO & Cl + CO_2) \\ \hline \end{array}$$

$$\text{net} \quad CO + 1/2\ O_2 \quad CO_2$$

Recognizing the possible importance of hydroxyl radicals, McElroy et al. (1973) considered two schemes, first proposed for the Martian atmosphere (McElroy and Donahue, 1972; Parkinson and Hunten, 1972):

$H + O_2 + M \quad HO_2 + M$ (R22)

$O + HO_2 \quad OH + O_2$ (R31) (II)

$CO + OH \quad CO_2 + H$ (R25)

---

net $CO + O \quad CO_2$

$H + O_2 + M \quad HO_2 + M$ (R22)

$1/2\ (2\ HO_2 \quad H_2O_2 + O_2)$ (R35) (III)

$1/2\ (H_2O_2 + h \quad 2\ OH)$ (R6)

$CO + OH \quad CO_2 + H$ (R25)

---

net $CO + 1/2\ O_2 \quad CO_2$

More recently Krasnopol'skii and Parshev (1980a,b) and the present authors independently considered the schemes:

$CO + Cl + M \quad COCl + M$ (R92)

$COCl + O_2 \quad CO_2 + ClO$ (R94) (IVa)

$1/2\ (ClO + ClO \quad Cl_2 + O_2)$

$1/2\ (Cl_2 + h \quad 2\ Cl)$ (R87)

---

net $CO + 1/2\ O_2 \quad CO_2$

$CO + Cl + M \quad COCl + M$ (R92)

$COCl + O_2 \quad CO_2 + ClO$ (R94) (IVb)

$1/2\ (ClO + ClO \quad Cl + ClOO)$

$1/2\ (ClOO + M \quad Cl + O_2 + M)$ (R89)

---

net $CO + 1/2\ O_2 \quad CO_2$

We may note that the effectiveness of the catalytic cycles I-IV depends critically on the abundance of trace amounts of radical species. In schemes I and IV great stability of the complexes ClOO and COCl towards thermal decomposition is required. Subsequent kinetic studies, to be elaborated in a later section, suggested that, with the exception of scheme II, all the above schemes are of limited application to the atmosphere of Venus.

The presence of COS and H_2S in the lower atmosphere of Venus was predicted by Lewis (1970) on geochemical grounds. The possibility of oxidation of reduced sulfur to oxidized sulfur compounds was recognized by Prinn (1971). Following the suggestion that the clouds of Venus are composed of sulfuric acid (Sill, 1972; Young and Young, 1973), it was recognized (McElroy et al., 1973; Prinn, 1973, 1975; Sze and McElroy, 1974; Wofsy and Sze, 1975) that the availability of O_2 could limit the production rate of H_2SO_4. Prinn (1973, 1975) proposed a scheme for oxidation of COS to H_2SO_4 using the O_2 derived from CO_2 photolysis:

$$\mathrm{COS + h \qquad CO + S(^1D)}$$

$$\mathrm{S(^1D) + M \qquad S + M}$$

$$\mathrm{S + O_2 \qquad SO + O} \qquad \text{(R46)} \quad \text{(V)}$$

$$\mathrm{SO + OH \qquad SO_2 + H} \qquad \text{(R53)}$$

$$\mathrm{SO_2 + HO_2 \qquad SO_3 + OH} \qquad \text{(R59)}$$

$$\mathrm{SO_3 + H_2O + M \qquad H_2SO_4 + M} \; . \qquad \text{(R64)}$$

This scheme can be roughly summarized as:

$$\mathrm{COS + 2\ O_2 + H_2O + (HO_x)}$$
$$\mathrm{CO_2 + H_2SO_4 + (HO_x)} \; ,$$

where the hydroxyl radicals HO_x play a crucial role as catalyst. Qualitative calculations performed by Prinn (1973, 1975) demonstrated that scheme V could indeed be a major path for destroying O_2 and producing H_2SO_4. However, COS has not been positively identified in the lower atmosphere (Hoffman et al., 1980a; Hoffman et al., 1980b; Oyama et al., 1980). Prinn (1971, 1973, 1975, 1978, 1979) argued that COS could be readily destroyed by

$$\mathrm{COS + S \qquad CO + S_2} \; .$$

Indeed, there is strong circumstantial evidence for the presence of polysulfur in the spectrum taken by Venera 11 and 12 below 38 km (Moroz et al., 1980; San'ko, 1980). This lends support to Prinn's argument. In this work we will not discuss the chemistry of COS.

The discovery of the first gaseous sulfur species, SO_2, on Venus (Barker, 1979) and its confirmation by Conway (1979), Stewart et al. (1979), and Esposito et al. (1979) led Winick and Stewart (1980) to examine the photochemistry of SO_2 in a fairly comprehensive model involving the interaction of chlorine, hydrogen, oxygen and sulfur compounds. The photochemistry of SO_2 is initiated by absorption of photons shortward of 2190Å (Okabe, 1978),

$$SO_2 + h \qquad SO + O \qquad\qquad (R9) .$$

The recombination reaction

$$SO + O + M \qquad SO_2 + M \qquad\qquad (R50)$$

is, however, extremely fast (Hampson, 1980) and hence photolysis of SO_2 does not always lead to net destruction. Oxidation of SO_2 to H_2SO_4 is, of course, a net sink. In addition to oxidation schemes using HO_x radicals (Prinn, 1973, 1975), Winick and Stewart (1980) recognized the importance of two new schemes:

$$\begin{array}{llll}
1/2\ (SO + h & S + O) & (R8) & \\
1/2\ (S + O_2 & SO + O) & (R46) & (VIa) \\
SO_2 + O + M & SO_3 + M & (R57) & \\
SO_3 + H_2O + M & H_2SO_4 + M & (R64) &
\end{array}$$

$$\begin{array}{ll}
\hline
\text{net} & SO_2 + 1/2\ O_2 + H_2O \qquad H_2SO_4
\end{array}$$

$$\begin{array}{rl}
1/2\ (\ SO_2 + h & \qquad SO + O\ ) \\
1/2\ (\ 2SO & \qquad SO_2 + S\ ) \\
1/2\ (\ S + O_2 & \qquad SO + O\ ) \\
SO_2 + O + M & \qquad SO_3 + M \\
SO_3 + H_2O + M & \qquad H_2SO_4 + M \\
\hline
\text{net} \quad SO_2 + 1/2\ O_2 + H_2O & \qquad H_2SO_4
\end{array} \qquad (VIb)$$

The Winick-Stewart model successfully reproduces the observed SO_2 distribution, with an appropriate choice of the eddy diffusivity profile. But the model predictions for the concentrations of CO and O_2 are about factors of 3 and 50, respectively, higher than those allowed by observations.

The large concentration of O_2 predicted by the Winick-Stewart model is surprising, especially since the authors have introduced two new powerful catalytic cycles for breaking the O-O bond:

$$\begin{array}{rll}
SO + h & \qquad S + O & \qquad (R8) \\
S + O_2 & \qquad SO + O & \qquad (R46) \quad (VIIa) \\
\hline
\text{net} \quad O_2 & \qquad 2\ O &
\end{array}$$

$$\begin{array}{lll} SO + SO \quad SO_2 + S & (R56) & \\ SO_2 + h \quad SO + O & (R9) & (VIIb) \\ S + O_2 \quad SO + O & (R46) & \end{array}$$

---

net $O_2 \quad 2\ O$

These cycles constitute a crucial part of the SO_2 oxidation schemes VIa and VIb. The reason for the high O_2 predicted by the model lies in the efficiency of the classic chlorine cycle for converting odd oxygen into molecular oxygen, first proposed for the Earth's stratosphere (Wofsy and McElroy, 1974; Stolarski and Cicerone, 1974; Molina and Rowland, 1974),

$$\begin{array}{lll} O + O_2 + M \quad O_3 + M & (R19) & \\ Cl + O_3 \quad ClO + O_2 & (R39) & (VIII) \\ ClO + O \quad Cl + O_2 & (R44) & \end{array}$$

---

net $2\ O \quad O_2$

An inspection of Figures 4b and 4c in Winick and Stewart (1980) reveals that, indeed, the effects of cycles VIIa and VIIb are nearly neutralized by cycle VIII.

Is the efficiency of cycle VIII, as described in Winick and Stewart (1980), unrealistic? Again, analogy with the chlorine chemistry in the Earth's stratosphere will illuminate the discussion. In the Earth's stratosphere the reaction ClO + NO competes with ClO + O (Logan et al., 1978) and can turn the chlorine cycle into a null cycle:

$$\begin{array}{llll} O + O_2 + M & O_3 + M & (R19) & \\ Cl + O_3 & ClO + O_2 & (R39) & (IX) \\ ClO + NO & Cl + NO_2 & (R110) & \\ NO_2 + h & NO + O & (R96) & \end{array}$$

---

net nothing

The potential role of nitrogen oxides in the atmosphere of Venus was discussed by Watson et al. (1979), who suggested the possible importance of the NO_x (= N, NO, NO_2, NO_3, HNO_2, HNO_3) reactions that can break the O-O bond:

$$\begin{array}{lll} NO + HO_2 & NO_2 + OH & (R109) \\ CO + OH & CO_2 + H & (R25) \\ H + O_2 + M & HO_2 + M & (R22)\ . \end{array}$$

However, in view of the probable low abundance of oxides of nitrogen in the atmosphere of Venus (Stewart et al., 1980; Scarf et al., 1980), it is unlikely that cycle IX and the reactions proposed by Watson et al. (1979) can play a major role (see discussion in later section). But there are analogs of these nitrogen reactions on Venus. Recently Clyne and MacRobert (1981) showed that the reaction,

$$ClO + SO \qquad Cl + SO_2 \qquad \text{(R55)},$$

is fast. Hence, we have a null chlorine cycle, in which SO plays the role equivalent to NO in cycle IX:

$$\begin{array}{llll}
O + O_2 + M & O_3 + M & \text{(R19)} & \\
Cl + O_3 & ClO + O_2 & \text{(R39)} & \text{(X)} \\
ClO + SO & Cl + SO_2 & \text{(R55)} & \\
SO_2 + h & SO + O & \text{(R9)} & \\
\hline
\text{net} & \text{nothing} & &
\end{array}$$

Since ClO and HO_2 are chemically alike, we shall argue that the reaction

$$HO_2 + SO \qquad OH + SO_2 \qquad \text{(R54)}$$

is also fast. We propose two new catalytic schemes for oxidizing CO and SO_2,

$$\begin{array}{lll}
H + O_2 + M & HO_2 + M & \\
1/2(SO + HO_2 & SO_2 + OH) & \\
1/2(SO_2 + h & SO + O) & \text{(XI)} \\
1/2(O + HO_2 & OH + O_2) & \\
CO + OH & CO_2 + H &
\end{array}$$

$$\text{net} \qquad CO + 1/2O_2 \quad CO_2$$

$$
\begin{array}{lll}
H + O_2 + M \quad HO_2 + M & (R22) & \\
SO + HO_2 \quad SO_2 + OH & (R54) & \\
SO_2 + h \quad SO + O & (R9) & (XII) \\
CO + OH \quad CO_2 + H & (R25) & \\
SO_2 + O + M \quad SO_3 + M & (R57) & \\
SO_3 + H_2O + M \quad H_2SO_4 + M & (R64) &
\end{array}
$$

$$CO + SO_2 + O_2 + H_2O \quad CO_2 + H_2SO_4$$

Winick and Stewart (1980) fixed the mixing ratio of H_2 to be 2×10^{-7}, a value first suggested by McElroy et al. (1973) and Sze and McElroy (1974) on the basis of thermodynamic considerations. Recent works, based on the Pioneer Venus mission (Hoffman et al., 1980; Kumar et al., 1981) preferred a much higher concentration of H_2 in the upper and lower atmosphere of Venus. The role of H_2 in the photochemistry of chlorine compounds is somewhat similar to that of CH_4 in the stratosphere of the Earth (Logan et al., 1978). The reaction,

$$Cl + H_2 \quad HCl + H \qquad (R38) ,$$

turns an active chlorine radical into a relatively inert form of chlorine.

However, there are important reactions that can reverse this process:

$$O + HCl \quad OH + Cl \qquad (R16)$$

$$H + HCl \quad H_2 + Cl \qquad (R21)$$

$$OH + HCl \quad H_2O + Cl \qquad (R27) .$$

One would expect, to first order, that the photochemistry is not sensitive to the abundance of H_2 (Sze and McElroy, 1974; Kumar et al., 1981). But this is not true in the updated models (Winick and Stewart, 1980; this work). A major loss of HO_x and ClO_x radicals is

$$Cl + HO_2 \quad HCl + O_2 \qquad (R41)$$

(Leu and DeMore, 1976). At low H_2 concentrations (- 0.1 ppm) $[Cl] >> [HO_2]$. But at high concentrations of H_2 (- 10 ppm) $[Cl] = [HO_2]$, and hence $R_{41} = k_{41}[Cl][HO_2]$ becomes more effective. Furthermore, SO_2 provides a heterogeneous loss of HO_x as is assumed in the Winick-Stewart model,

$$SO_2 + OH + M \quad HSO_3 + M \qquad (R58)$$

but <u>not</u> in Sze and McElroy (1974) and Prinn (1973, 1975). If Winick and Stewart (1980) had used the value of H_2 suggested by Kumar et al. (1981), the concentration of free chlorine would have been lower by 2 orders of magnitude, thus avoiding the catastrophe caused by cycle VIII.

There can be additional heterogeneous sinks for HO_x and ClO_x radicals in the lower stratosphere. McElroy (private communication, 1973) and Sze and Smyth (1979) suggested that

$$SO_2 + H_2O_2 \quad H_2SO_4 \text{ (heterogeneous)} \qquad \text{(R60)}$$

could oxidize SO_2 and destroy HO_x. Stratton et al. (1979) suggested that

$$Cl + SO_2 + M \quad ClSO_2 + M \qquad \text{(R61)}$$

could be a sink for ClO_x.

The detailed mechanisms for heterogeneous losses implied by R58, R60 and R61 have never been elucidated. The works of Davis et al. (1979) and Friend et al. (1980) offer plausible arguments that R58 results in the loss of a HO_x for <u>terrestrial</u> environments. We shall examine the validity of these arguments for conditions appropriate to Venus.

The photochemistry of SO_2 is further complicated (and enriched) by the chemistry of $(SO)_2$ dimer, formed by

$$SO + SO + M \quad (SO)_2 + M \qquad \text{(R79)} ,$$

(Herron and Huie, 1980). The structure of the dimer is known (Lovas et al., 1974). The OS-SO bond strength has been estimated to be 30-70 kcal/mol (Benson, 1978; Herron and Huie, 1980). The homogeneous chemistry of $(SO)_2$ can be summarized by two catalytic cycles:

$SO + SO + M \quad (SO)_2 + M$ (R79)

$(SO)_2 + SO \quad SO_2 + S_2O$ (R84) (XIII)

$S_2O + O \quad 2SO$ (R80)

---

net $SO + O \quad SO_2$

$SO + SO + M \quad (SO)_2 + M$ (R79)

$(SO)_2 + O \quad S_2O + O_2$ (R83) (XIV)

$S_2O + O \quad 2SO$ (R79)

---

net $O + O \quad O_2$

Cycle XIII catalytically recombines SO and O and can be interpreted as an increase in the rate coefficient for

$SO + O + M \quad SO_2 + M$ (R50) ,

or decrease in the photolysis rate of SO_2

$SO_2 + h \quad SO + O$ (R9) .

The net result is the suppression of the cycles VIa, b, XI and XII. Cycle XIV is based on analogy with cycle XIII and results in catalytically recombining oxygen atoms.

Nair et al. (1963) suggested that S_2O is the anhydride of thiosulfurous acid ($H_2S_2O_2$). Friend (1981, private communication)[+] suggested that $(SO)_2$ could be the anhydride of thiosulfuric acid ($H_2S_2O_3$). We propose two speculative schemes:

$$\begin{array}{lll}
3(SO_2 + h \quad SO + O) & (R9) & \\
2SO + M \quad (SO)_2 + M & (R79) & \\
(SO)_2 + SO \quad S_2O + SO_2 & (R84) & (XV) \\
S_2O + H_2O \quad H_2S_2O_2 & (R81) & \\
3(SO_2 + O + M \quad SO_3 + M) & (R57) & \\
3(SO_3 + H_2O \quad H_2SO_4) & (R64) & \\
\hline
\end{array}$$

$$\text{net} \qquad 5SO_2 + 4H_2O \quad H_2S_2O_2 + 3H_2SO_4$$

$$\begin{array}{lll}
2(SO_2 + h \quad SO + O) & (R9) & \\
2SO + M \quad (SO)_2 + M & (R79) & \\
(SO)_2 + H_2O \quad H_2S_2O_3 & (R85) & (XVI) \\
2(SO_2 + O + M \quad SO_3 + M) & (R57) & \\
2(SO_3 + H_2O \quad H_2SO_4) & (R64) &
\end{array}$$

[+] We are also indebted to J. P. Pinto for drawing our attention to thiosulfuric acid. It should be noted that going from $(SO)_2$ to $H_2S_2O_3$ involves a major rearrangement of the sulfur and oxygen atoms.

$$4SO_2 + 3H_2O \qquad H_2S_2O_3 + 2H_2SO_4$$

The reaction,

$$S_2O + S \qquad S_2 + SO \qquad\qquad (R80)$$

is probably as fast as R79 and leads us to consider another speculative scheme,

$$\begin{array}{rll}
4(SOo_2 & SO + O) & \\
2(2SO + M & S_2O_2 + M) & \\
2(S_2O_2 + SO & S_2O + SO_2) & \\
S_2O + h & S + SO & \qquad (XVII) \\
S + S_2O & S_2 + SO & \\
4(SO_2 + O + M & SO_3 + M) & \\
4(SO_3 + H_2O & H_2SO_4) &
\end{array}$$

$$6SO_2 + 4H_2O \qquad 4H_2SO_4 + S_2$$

The significance of schemes XV-XVII is twofold. First, these are the first known schemes for producing H_2SO_4 from SO_2 without using CO_2 derived oxygen. Secondly, atmospheric photochemistry can start with SO_2 (oxidation state = 4) and segregate it into a more oxidized sulfur compound, H_2SO_4(oxidation state = 6), and reduced sulfur compounds, $H_2S_2O_2$ (oxidation state = 1), $H_2S_2O_3$ (oxidation state = 2) and S_2 (oxidation state = 0). Similar systems leading segregation of oxidized and reduced compounds have been investigated by Yung and McElroy (1979), Pinto et al. (1980) and McElroy et al. (1980).

Since so many uncertainties remain, we extend our discussion to include the chemistry of a miscellaneous set of compounds that are not important from the present point of view, but may become important, should major revisons in the chemical kinetics or observations be made in the future. N_2 and NO have been detected on Venus (Oyama et al., 1979; Stewart et al., 1979; Feldman et al., 1979; Stewart and Barth, 1979). The photochemistry of odd nitrogen NO_x (N, NO, NO_2, NO_3, HNO_2 and HNO_3) is similar to that on Mars (Yung et al., 1977). An understanding of the NO_x chemistry on Mars and Venus today may advance our understanding of the nitrogen chemistry in the primitive atmosphere of the Earth (Yung and McElroy, 1979). To first order, NO_x chemistry is not important for the Venus stratosphere and we include only a brief discussion. The chemistry of COS and H_2S involves too intimately the chemistry of the lower atmosphere and can only be treated adequately in another paper. We refer the reader to previous works on the subject of Venus (Prinn, 1973, 1975; Sze and Smyth, 1979) and recent works on Earth's atmosphere (McElroy et al., 1980; Sze and Ko, 1980).

We have briefly discussed the photochemistry of the atmosphere of Venus in terms of 17 major chemical schemes and cycles summarized in Table 2. The discussion reveals at least three aspects of Venus photochemistry where previous treatments are inadequate: (1) the photochemistry of SO; (2) the sensitivity of photochemical models to the abundance of H_2; (3) the role of heterogeneous processes in the lower stratosphere. This paper will concentrate on these aspects. A critical discussion on chemical kinetics will be given, followed by modeling results and a comparison between the stratospheric chemistry of Venus and Earth, and a discussion on future experiments capable of distinguishing various models.

2. Photochemistry and Chemical Kinetics

Table 3a summarizes the most important reactions for the major compounds of carbon, oxygen, hydrogen, chlorine and sulfur, along with preferred values of their rate coefficients, to be used in the standard model, model A. Tables 3b, 3c, and 3d include additional reactions of more speculative nature, or lesser importance, to be explored in alternative models, models B, C and D, respectively. Our set of reactions encompasses most of those considered in previous works, but has been critically assessed and updated. In general, the chemistry of carbon, oxygen, hydrogen and chlorine species is well defined, due, in part, to recent progress in the chemistry of the Martian atmosphere (McElroy and Donahue, 1972) and the Earth's stratosphere (NAS, 1976; Logan et al., 1978; NASA, 1977, 1980). Our understanding of the chemistry of sulfur is still at a rather primitive stage, even for the Earth's atmosphere (Crutzen 1976; Turco et al., 1979; Sze and Ko, 1980). Unfortunately, as we will show, the photochemistry of the atmosphere of Venus is, to first order, critically controlled by the coupling between sulfur compounds and the hydroxyl and chlorine species (this is not true in the Earth's stratosphere, where the relative abundance of sulfur compounds is three orders of magnitude lower than that on Venus).

Most reactions in Table 3a have recently been evaluated by Hampson and Garvin (1978), Hampson (1980), Baulch et al. (1980) and DeMore et al. (1981), and the reader is referred to these publications for a critical discussion. The rate constants for the following three-body reactions,

$$2\,O + M \qquad O_2 + M \qquad \text{(R17)}$$

$$O_2 + O + M \qquad O_3 + M \qquad \text{(R19)}$$

$$H + O_2 + M \qquad HO_2 + M \qquad \text{(R22)}$$

$$H + H + M \qquad H_2 + M \qquad \text{(R24)}$$

$$SO_2 + O + M \qquad SO_3 + M \qquad \text{(R57)}$$

$$SO_2 + Cl + M \qquad ClSO_2 + M, \qquad \text{(R61)}$$

have not been measured for $M = CO_2$. We have taken the rate coefficients to be twice the corresponding values for $M = N_2$, to account for the greater efficiency of CO_2 as a third body.

The photochemistry of SO plays an essential role in breaking the O-O bond in schemes Va,b and VI (see Table 2). The cross-sections for SO photolysis,

$$SO + h \qquad S + O \qquad \text{(R8)} ,$$

have recently been measured at JPL by Phillips (1981). The results are close to those estimated by Winick and Stewart (1980) on the basis of analogy between the O_2 and SO Schumann-Runge bands (Okabe, 1978; McGarvey and McGrath, 1964; Colin, 1969; Krupenie, 1972; Smith and Liszt, 1971), and thus confirm the importance of scheme Va. The rate coefficient for

$$2\,SO \qquad SO_2 + S \qquad \text{(R56)}$$

is probably an order of magnitude faster than that assumed by Winick and

Stewart (1980), as suggested by Herron and Huie's (1980) experiment, and thus scheme Vb could be even more important than was thought.

The success of the schemes VIa,b critically depends on the bond breaking reaction R46, $S + O_2$, which is the only sink for S in our standard model A (Table 3a). The reaction,

$$S + CO_2 \qquad CO + SO \qquad H = 2.6 \text{ kcal/mol}$$

is only slightly endothermic, and could be important even if its rate coefficient were as low as 10^{-18} cm^3 s^{-1}. However, until further experiments are performed, we consider the breaking of the C-O bond by S unlikely and we do not include this reaction in our chemical schemes.

Clyne and MacRobert (1981) reported a fast rate coefficient for

$$SO + ClO \qquad SO_2 + Cl \qquad\qquad (R55) \text{ ,}$$

$k = 2.3 \times 10^{-11} cm^3 s^{-1}$. Since the bond strengths for Cl-O and HO-O are both equal to 64 Kcal/mol, reactions involving HO_2 always bear great similarity to isoelectronic reactions involving ClO, as demonstrated by the pair of reactions,

$$NO + ClO \qquad NO_2 + Cl \qquad k_{110} = 1.8 \times 10^{-11} cm^3 s^{-1}$$

$$NO + HO_2 \qquad NO_2 + OH \qquad k_{109} = 8.4 \times 10^{-12} cm^3 s^{-1}$$

and the pair,

$$O + ClO \qquad O_2 + Cl \qquad k_{44} = 5.0 \times 10^{-11} cm^3 s^{-1}$$

$$O + HO_2 \qquad O_2 + OH \qquad k_{31} = 3.1 \times 10^{-11} cm^3 s^{-1}$$

(DeMore et al., 1981). We argue that the reaction,

$$SO + HO_2 \qquad SO_2 + OH \qquad (R54)$$

should be as fast as R55, and could provide a major pathway for breaking the O-O bond (schemes XI and XII). The alternative branch,

$$SO + HO_2 \qquad HSO + O_2,$$

is probably slow, and is most probably followed by

$$O + HSO \qquad OH + SO.$$

This would result in recycling HO_x radicals, and would be of secondary importance even if the branching ratio were to equal unity. The reaction R54 seems to have been first noted by Sze and Smyth (1979) in an unpublished NASA report. However, the authors made an unrealistic estimate for the rate coefficient, $k_{54} = 1 \times 10^{-14} cm^3 s^{-1}$.

The efficiency of the catalytic scheme for oxidation of SO_2,

$$SO_2 + HO_2 \qquad SO_3 + OH \qquad (R59),$$

as considered by Prinn (1973, 1975) and Winick and Stewart (1980), is probably overestimated. The recent works of Graham et al. (1979) and Sander and Watson (1981) strongly suggest that $k_{59} < 10^{-18} cm^3 s^{-1}$, which is orders of magnitude slower than that preferred by the previous authors. The reaction,

$$SO_2 + OH + M \qquad HSO_3 + M \qquad\qquad (R58) ,$$

has been extensively studied (see Baulch et al., 1980) in connection with homogeneous gas phase oxidation of SO_2 to sulfate. The recent works of Davis et al. (1979) and Friend et al. (1980) suggested that the ultimate fate of HSO_3 in the atmosphere is formation of H_2SO_4 or related compounds. It is assumed that the hydroxyl radical in reaction R58 is consumed and not recycled. The possibility of recycling HO_x was noted by Turco et al. (1979), who, without discussing a detailed mechanism, proposed a net reaction equivalent to

$$SO_2 + OH \qquad SO_3 + H.$$

The reaction R58 is probably not as important as schemes Va,b and VI for oxidation of SO_2 on Venus, but could be important as a sink for HO_x. In addition, there are similar reactions involving HO_x and ClO_x,

$$SO_2 + H_2O_2 \qquad H_2SO_4 \text{ (heterogeneous)} \qquad (R60)$$

$$SO_2 + Cl + M \qquad ClSO_2 + M \qquad (R61)$$

An investigation of heterogeneous reactions is not the main thrust of this work. Removal of gas molecules by aerosols is simply modeled as a net loss rate given by $J = 1/4 \quad vAN_a$, where N_a = number density of aerosols (cm^{-3}), A = mean surface area of aerosol (cm^2), v = thermal velocity of gas molecule and   = sticking coefficient. The profiles for N_a and A are taken from Knollenberg and Hunten (1980). The sticking coefficients are based on Baldwin and Golden (1979) and Golden (1981, private communication): $_{H\ O}$ = 1.6×10^{-3}, $_{radicals} \simeq \ _{OH} = 1 \times 10^{-4}$. It can be shown that heterogeneous losses are not important for most species considered in our model, with the possible exception of R58, R60 and R61. In Table 3a (model A) we assumed, for simplicity, that all these three reactions result in net destruction of HO_x or ClO_x.

An alternative set of reactions involving HSO_3 are given in Table 3b. The crucial reactions that can retrieve the HO_x radical tied by HSO_3 is

$$HSO_3 + O \quad OH + SO_3 \qquad (R66)$$

and

$$HSO_3\ H_2O + O \quad OH + H_2SO_4. \qquad (R72)$$

The rate coefficient for this type of hydrogen abstraction reaction correlates with exothermicity, and on this basis we estimate a value of $1 \times 10^{-11} cm^3 s^{-1}$ for the rate coefficients for R66 and R72. We have little information on the thermodynamics and chemical kinetics of C SO_2. We assume that its properties are similar to HSO_3.

The recent experiment by Herron and Huie (1980) suggested that the dimer $(SO)_2$, formed by

$$2\ SO + M \quad (SO)_2 + M \qquad (R79)$$

is fairly stable. An analysis of their experiment suggests that the rate coefficient for decomposition by collision,

$$(SO)_2 + M \qquad 2\ SO + M \qquad\qquad (R82)\ ,$$

must be less than 1 x $10^{-20} cm^3 s^{-1}$. The fate of the dimer is of great importance to the atmosphere of Venus. Herron and Huie (1980) suggested

$$(SO)_2 + SO \qquad S_2O + SO_2 \qquad\qquad (R84)\ .$$

S_2O is readily removed by reaction with O and S,

$$S_2O + O \qquad 2SO \qquad\qquad (R79)$$

$$S_2O + S \qquad S_2 + SO \qquad\qquad (R80)$$

(Stedman et al., 1974) or by photolysis

$$S_2O + h \qquad S + SO \qquad\qquad (R77)$$

(Okabe, 1978). Since the bond strengths for OS-O (131 kcal/mol) and O-O (119 kcal/mol) are similar, we postulate that the reaction

$$(SO)_2 + O \qquad S_2O + O_2 \qquad\qquad (R83)$$

is as fast as R84. The net result of these sets of reactions can be visualized in terms of the three cycles XIII-XVI.

Table 3c summarizes a speculative scheme involving reactions with $(SO)_2$. The most interesting aspect of this scheme is the possibility that S_2O is the anhydride of thiosulfurous acid ($H_2S_2O_2$) (Nair et al., 1963), that $(SO)_2$ could be the anhydride of thiosulfuric acid ($H_2S_2O_3$) and the production of S_2. Unfortunately, so little is known about this system that Table 3c presents only a speculation.

Table 3d includes the chemistry of compounds of lesser importance. But the judgement on the relative importance of these compounds is somewhat arbitrary, and reflects the current status of our knowledge (or ignorance). Hence, Table 3d is useful for future reference. We will briefly discuss the chemistry of COCl. COCl is formed by

$$CO + Cl + M \qquad COCl + M \qquad\qquad (R92)\ .$$

It is destroyed by thermal decomposition,

$$COCl + M \qquad CO + Cl \qquad\qquad (R93)\ ,$$

and by bond breaking reaction with O_2,

$$COCl + O_2 \qquad CO_2 + ClO \qquad\qquad (R94)\ .$$

The efficiency of schemes IVa,b critically depends on the magnitude of the quantity

$$E =$$

According to the estimates of Krasnopol'skii and Parshev (1980a,b), $k_{92} = 3 \times 10^{-33}$ cm^6 s^{-1}, $k_{93} = 1 \times 10^{-12} e^{-3200/T}$ cm^3 s^{-1} and $k_{94} = 2 \times 10^{-14}$ cm^3 s^{-1}; and hence $E = 2.2 \times 10^{-29}$ at room temperature. Our own measurements, to be published elsewhere, suggested that E is probably 20 times smaller. Thus the high efficiency for schemes (IVa,b) is certainly overestimated by Krasnopol'skii and Parshev (1980). The nitrogen chemistry shown in Table 3d is straightforward, and is based on McConnell and McElroy (1973), Yung et al., (1977) and Yung and McElroy (1979).

3. Model Assumptions and Approach

The model atmosphere is taken from Winick and Stewart (1980). Our model extends from 58 to 110 km. The concentrations of H_2O and HCl are fixed at constant mixing ratios of 1×10^{-6} and 4×10^{-7}, respectively (see Table 1). The mixing ratio of H_2 equals 2×10^{-5} in the standard models, but lower values are explored in alternative models. The one-dimensional continuity equations are rigorously solved for all major species with appropriate boundary conditions listed in Table 4. It is not necessary to group the species into families. We use a finite difference iterative algorithm with 2 km resolution (Logan et al., 1978; Allen et al., 1981), except at the boundaries, where the resolution is 0.4 km. The convergence criterion is the requirement that successive iterations yield solutions differing by less than one part in 10^4.

The solar flux between Lyman- and 4000Å is taken from Ackerman (1971) and Mount et al. (1981) and averaged over appropriate 50Å intervals. In the spectral region where the two sets of data overlap, Mount et al.'s (1981) data are preferred. The dissociation cross-sections for CO_2 is taken from Shemansky (1972), with temperature dependence correction based on DeMore and Patapoff (1972),

$$P(\ ) = 0.5 + 5 \times 10^{-3}(\ \ - 1740\text{Å})/1640\text{Å} \leq \qquad \geq 1900\text{Å}$$

$P(\ ) = P(1900Å) \qquad 1900Å) \leq \qquad \leq 2040Å$.

We choose to apply a uniform temperature correction at 250 °K. Beyond 1900Å, there is actually no laboratory data. Rather than extrapolating P( ) to alarming values, we set all the correction factors beyond 1900Å to equal that at 1900Å. The additional dissociation of O_3 at Chappuis bands is taken into account by adding a mean dissociation rate $3.3 \times 10^{-4} s^{-1}$ to J_{5b} at all altitudes. The absorption cross-sections of SO_2 have not been measured at temperatures appropriate to the stratosphere of Venus. We recently undertook these measurements at JPL (DeMore et al., 1981). At 250°K, the cross-sections are about a factor of 2 lower than those at room temperature. In this work we adopt the JPL cross-sections measured at 250°K. For dissociation cross-sections we use quantum yields estimated from the fluorescence spectra given by Okabe (1971). Since the cross-sections for SO_2 and SO near 2000Å are highly structured, we subdivide the region 1800-2320Å into 10Å intervals. The averaged solar flux and cross-sections for CO_2, SO_2, HCl and SO over this fine grid are given in Table 5. The mean dissociation rates $J_i(s^{-1})$ for these species are calculated by the following formula:

where = incident normal solar flux at Venus

= optical depth =

= average cosine of solar zenith angle

and the other symbols have their usual meanings. To simulate midlatitude insulation, we set = 2/3. In the lower stratosphere between 58 and 70 km, the solar radiation field is further attenuated by absorption by aerosols. This is roughly taken into account by reducing the incident solar flux by a transmission factor,

$$T(z) = e^{-(70-z)/10} \qquad 58 \text{ km} \lesssim z \lesssim 70 \text{ km}$$

$$T(z) = 1 \qquad z \gtrsim 70 \text{ km}.$$

This choice of T(z) has been guided by the ultraviolet photometric observations of Ragent and Blamont (1980) over this altitude range.

The eddy diffusivity profile in the upper atmosphere near the homopause (~140 km) has been determined by Von Zahn et al. (1979), who proposed the expression

$$K(z) = 2 \times 10^{13}/ \quad M \quad cm^2 \; s^{-1} ,$$

where M = number density of ambient atmosphere in molecules cm^{-3}. Between 58 and 110 km K(z) has not been determined, and we are guided only by the theoretical work of Prinn (1975) and the measurements of thermal structure by Seiff et al. (1980). Figure 1a gives the temperature lapse rate derived from the day probe data of Seiff et al. (1980) by Pechmann (1981, private communication). As pointed out by Seiff et al. (1980), the region of the atmosphere above the cloud tops exhibits a stable lapse rate and should be appropriately designated the principal Venus stratosphere. Hence the trend of Von Zahn et al.'s (1979) K(z) in the lower stratosphere must be correct. By trial and error, we arrive at profile A in Figure 1b for our standard model, model A. The high value, 3×10^5 cm^2 s^{-1}, around 70 km is essential for ensuring rapid downward transport of O_2 to the lower atmosphere, and thus keeping its mixing ratio at about or below 1×10^{-6}. The sharp decrease between 70 and 58 km is needed for reproducing the correct scale height of SO_2 around 70 km, and for maintaining a reasonably high abundance of CO above the cloud tops. Since profile A seems somewhat artificial, we propose aother possibility, profile C, to be used in model C.

We consider four models. The assumptions are summarized in Table 6. Model A adopts the set of reactions given in Table 3a. The mixing ratio of H_2 equals 2×10^{-5} in the standardd model, but a range of other concentrations is explored. Model B adopts an additional set of reactions involving HSO_3, as listed in Table 3b. Model C pursues the consequences of $(SO)_2$ dimer chemistry. Model D treats a miscellaneous set of reactions of potential importance to the chemistry of the stratosphere.

4. Results and Discussion

The results for models A-D will be separately discussed in the following paragraphs. To facilitate comparisons with previous works, we cross-reference a selected set of the crucial parameters and rate coefficients in Table 7. All rate coefficients have been evaluated at 250°K. The large differences between the various models reflect the progress that has been made in the past decade, and the uncertainties that remain.

Model A

Altitude profiles for the concentrations of CO, O_2 and SO_2, as predicted by model A, and their comparisons with observations are presented in Figure 2. The computed abundance of CO in the lower stratosphere is somewhat lower than that suggested by the infrared data of Connes et al. (1981), but consistent with the microwave data of Schloerb et al. (1980) and Wilson et al. (1981). But the microwave measurements are not reliable in the lower parts of the atmosphere and we must put more weight on the infrared data. There are three reasons why we have too little CO: (a) the cross-sections for CO_2 photolysis at 250°K, adopted in the model, are lower than those at room temperature by about a factor of 2; (b) our model assumes a high concentration for H_2, which results in a high concentration of OH, of order 10^6 cm^{-3}; (c) we choose an eddy diffusion coefficient at the lower boundary $K = 3.5 \times 10^4$ cm^2 s^{-1}.

Reaction rates for the major reactions involved in the production and consumption of oxygen, R1 $CO_2 + h$, R25 $CO + OH$ and R57 $SO_2 + O$, are given in Figure 3. A detailed inventory, tracing through the budgets and flows of the major species, are shown in Figures 4a and Figure 4b. In Figure 4b, the column abundances above the cloud tops are given in units of 1×10^{18} molecules cm^{-2}. The flux units are 10^{12} molecules cm^{-2} s^{-1}. Figure 4b reveals the intimate relations between the chemistry of the upper atmosphere, driven by photochemistry, and the lower atmosphere, dominated by thermochemical equilibrium. The mean lifetimes of the gases CO, O_2 and SO_2, in the upper atmosphere are 2.9×10^7, 6×10^6 and 1.3×10^6 sec, respectively. The column density of H_2SO_4 above 58 km, as implied by the data of Knollenberg and Hunten (1980), is 7×10^{18} cm^{-2}. The Stokes falling velocity for particles of radius equal to 1 is 2.7×10^{-2} cm s^{-1} and must be added to the eddy velocity. The estimated downward flux of H_2SO_4 is 1×10^{12} cm^{-2} s^{-1}. Our column production rate for H_2SO_4 is somewhat larger, but probably within the limits of the uncertainties of the measurements. We have assumed a constant mixing ratio for H_2O. For production rates of order of this magnitude or higher, the availability of H_2O may be a limiting factor, and may account for the lack of horizontal homogeneity in the SO_2 abundances (Esposito and Gates, 1981). The predicted concentration of O_2 is in reasonable agreement with the observed upper limit quoted by Traub and Carleton (1974). The predicted ratio between the column abundances of CO and O_2 is about 10, considerably lower than the lower limit of 45 implied by the combination of the data by Connes et al. (1968) and Traub and Carleton (1974).

Altitude profiles for the major HO_x (H, OH, HO_2, H_2O_2) and ClO_x (Cl, ClO) species are presented in Figure 5. A schematic diagram showing the sources, sinks and partitioning between the HO_x and ClO_x species is given in Figure 6a. Reaction rates for the major reactions that produce HO_x and ClO_x, R2 HCl + h and R16 O + HCl and major reactions that destroy HO_x and ClO_x, R41 Cl + HO_2, R58 SO_2 + OH, R61 SO_2 + Cl and R60 H_2O_2 + SO_2 are given in Figure 7. Reaction rates for R38 Cl + H_2, R21 H + HCl and R27 OH + HCl, which determine the partitioning between HO_x and ClO_x are given in Figure 8. The concentration of ClO_x in our model is much lower than those in Sze and McElroy (1974), mainly due to the larger rate coefficient for R41 (see Table 7). The HO_x concentrations are much higher than those given by Winick and Stewart (1980). The main reason is the higher abundance of H_2 in our model. Figure 9 shows a sensitivity study of the abundances of the major species CO, O_2, SO_2, OH and ClO as a function of H_2 mixing ratio, while keeping all other parameters fixed. As f_H is decreased towards 0.1 ppm, we approach the solution of Winick and Stewart (1980). Hence the higher abundance of H_2 is essential for suppressing the concentration of ClO_x (and hence cycle VIII), thus bringing the predicted concentration of O_2 into agreement with observations.

The concentrations of oxygen species O, O(^{1}D), O_2 and O_3 are given in Figure 10. A schematic diagram summarizing the relation between the oxygen species is given in Figure 4b. Reaction rates for reactions leading to the formation of the O-O bond, R17 O + O + M, R28 O + OH and R44 O + ClO, and those leading to the breaking of the O-O bond, R46 S + O_2 and R54 SO + HO_2, are given in Figure 11. It can be seen that R54, first postulated in this paper, is extremely important. The reactions R17 O + O + M, R31 O + HO_2, R39 O_3 + Cl and R44 O + ClO are exothermic enough to produce an O_2 molecule in the excited ^{1} state. However, a new O-O bond is formed only in reactions R17, R31 and R44. The quantum yield for producing an $O_2(^1\ )$ in R17 has been estimated to be about 30% by Ogryzlo (1981, private communication), in agreement with the quantum yield obtained by Black and Slanger (1981) for recombination of O atoms on pyrex glass. In our computation we assume a quantum yield of 30% for producing $O_2(^1\ )$ for R17, R31 and R44. If the quenching rate coefficient is 1 x 10^{-20} (Noxon et al., 1976; Traub et al., 1979; Connes et al., 1979) only production above 88 km will contribute to the airglow observed by Connes et al. (1979). The column emission rates of $O_2(^1\ )$ $O_2(^3\ )$ at 1.27 for R17, R31 and R44 are 3 x 10^{11}, 1.6 x 10^{12} and 4 x 10^{10} cm^{-2} s^{-1}, respectively, giving a total emission rate of 5 x 10^{11} cm^{-2} s^{-1} or 0.5 MR. This value should be compared with the observed brightness of 1.5 and 1.2 MR on the dayside and nightside, respectively (Connes et al., 1979). In the Earth's atmosphere, the dayglow at 1.27 is about 30 MR, and is dominated by contributions from

$$O_3 + h \quad O_2(^1\ ) + O(^1D) \qquad (R5a) .$$

The nightglow is about 100 kR, arising most probably from the similar reactions R17, R31 in the mesosphere. Connes et al. (1979) recognized that the lack of a large contrast in the Venusian dayglow and nightglow can be used to set an upper limit to the abundance of O_3. In our model, the column abundance of O_3 is 2.2 x 10^{15} cm^{-2}, and the additional contribution to the dayglow by R5a is 0.3 MR, and hence predicts a slightly higher difference bewteen dayglow and nightglow.

Altitude profiles of the major sulfur species S, SO, SO_2 and SO_3 are shown in Figure 12. A schematic diagram given in Figure 4C shows how the sulfur species are partitioned. The speculative chemistry involving the dimer $(SO)_2$ is not considered in this model. The major reactions that control the cycling between SO_2 and SO are given in Figure 13: R9 SO_2 + h , R50 SO + O + M, R54 SO + HO_2, R55 SO + ClO and R56 SO + SO. Figure 14 gives the major reactions that control the cycling between SO and S: R8 SO + h , R46 S + O_2 and R56 SO + SO.

We can gain further insight into model A by deriving and examining a set of simple analytic solutions that can approximate the numerical solutions discussed in the previous sections. Inspection of Figure 3 suggests that the chemistry in the stratosphere of Venus can be roughly divided into two distinct regions. In the upper stratosphere near and above 70 km, the dominant chemistry is CO_2 recombination, catalyzed by HO_x. In the lower stratosphere between 60 and 70 km, SO_2 oxidation to H_2SO_4 is the primary process. The two regions are, to first order, decoupled from each other, at least for the short-lived species.

We shall make the approximation that in the upper stratosphere the concentrations of the long-lived species CO_2, CO, O_2, H_2 and HCl are controlled by transport. Inspection of Figure 6a and b enables us to write the following approximate relations for the partitioning of the HO_x and ClO_x radicals:

Balancing the production and loss of HO_x and ClO_x , we have,

$$J_2[HCl] = k_{41}[Cl][HO_2] \qquad (5)$$

Using (1) - (5) we can express all the radicals in terms of [OH],

where

The net source of oxygen is CO_2 photolysis (R1). The sinks for oxygen in this region of the atmosphere are CO_2 oxidation by OH (R25), and production of O_2 by R17, R28 and R44. Hence, we have

$$k_{25}[CO][OH] + 2\,k_{17}\,M\,[O]^2 + 2\,k_{28}[O][OH]$$
$$+ 2\,k_{44}[ClO][O] = J_1[CO_2]\ . \qquad (13)$$

Equation (13) can be expressed in terms of [OH] alone using (6) - (10),

$$k_{25}[CO][OH] + 2A(k_{28}+Bk_{44})[OH]^3 + 2A^2k_{17}M[OH]^4$$
$$= J_1[CO_2] \qquad (14)$$

Equation (14), a quantic algebraic equation in one unknown, can be solved analytically, and the answer closely reproduces the numerical calculation. However, the algebraic expressions are somewhat unwieldly and not particularly illuminating. All the essential physics is actually contained in equation (14), which describes the fate of CO_2 derived oxygen in the upper stratosphere. Note that from (11) and (12) the coefficients A and B are both inversely proportional to the concentration of H_2. At high H_2 concentrations, the balance in equation (14) is between the first term on the LHS and the RHS, and most of the oxygen is consumed by CO_2 recombination. At low concentrations of H_2, the balance in equation (14) is between the second, third and fourth terms on the LHS with the RHS. In this case, CO_2 recombination is suppressed, and the fate of atomic oxygen is to recombine to form O_2.

In the lower stratosphere, from 58 to about 70 km, the photochemistry is dominated by that of SO_2. We can ignore the chemistry of CO_2, HO_x and ClO_x, except for the downward transport of O_2. The distribution of SO_2 in the lower stratosphere is determined by diffusion from the lower atmosphere, and photochemical conversion to H_2SO_4. The equations governing SO_2 are,

where n = number density of SO_2 (cm^{-3})

= flux (cm^{-2} s^{-1})

H = mean atmospheric scale height (cm)

K = eddy diffusion coefficient (cm^2 s^{-1})

L = irreversible loss rate coefficient (s^{-1})

If we assume that K, H and L are constants (as a rough estimate), equations (15) and (16) can be solved in closed form,

$$n(Z) = n(Z_o)\ e^{-(Z-Z_o)/H^*} \qquad (17)$$

$$(Z_o) = Kn(Z_o) \qquad (18)$$

where

$$Z_o = 58 \text{ km}$$

It is clear that the effective scale height of SO_2, H^*, reflects the relative importance between chemistry and transport,

$$\text{line } H^* = H \qquad (20)$$

line H* =

Inspection of Figure 6c shows that cycling between SO_2 and SO is adequately described by

$$J_9[SO_2] = k_{50}[SO][O] + k_{56}[SO]^2 \qquad (22)$$

Since the simple sulfur chemistry in Table 3a allows for breaking the O-O bond by R46, S + O_2, but contains no reaction for forming the O-O bond, we can assume that every O-O bond that is broken by R46 leads to the formation of SO_3 (and eventually H_2SO_4),

$$k_{46}[S][O_2] = J_8[SO] + k_{56}[SO]^2 \qquad (23)$$

$$= k_{57}[SO_2][O] \qquad (24)$$

In arriving at (23) and (24), we have made two additional assumptions that R49, SO + HO_2, and that the oxidation of SO_2 is not limited by O_2 supply. The first assumption is fairly good near the cloud tops. The second assumption will be critically examined later. Combining (22) - (24), we have one equation for [SO],

This is a cubic equation in [SO] and can be solved analytically. But the algebraic expressions are complicated and not illuminating. The solution is particularly simple if the first term on the LHS dominates (this is true above 65 km). Then, we have,

A similar expression can be derived for [0]. We can now evaluate the loss rate of SO_2,

$$L[SO_2] = k_{57}[SO_2][O]$$

$$= J_8[SO]$$

The algebra is much more complicated if we have to solve (25) exactly, but the essential physics is illustrated by the simpler solution (27). Equation (27) can be used with equations (19) and (17) to determine the vertical profile of SO_2. That the rate of SO_2 destruction is independent of the concentrations of O and O_2, as implied by (25), is somewhat surprising, but is the direct consequence of the assumption that R46, $S + O_2$, is the only sink for S, a most reasonable assumption. But this implies that $_o$, the downward flux of O_2 from the upper stratosphere, must be such that,

$$dz\ L\ [SO_2] = 2\ _o \qquad (28)$$

Hence, we need a high eddy diffusion coefficient at around 70 km to insure the rapid transport of O_2 to the lower atmosphere. Within the framework of the chemical model Table 3a, we are forced into a solution with high rate of SO_2 oxidation. No amount of fine tuning, with the eddy diffusivity profile, for instance, can produce a radically different solution.

We are now in a position to critique the weaknesses of model A. First, the predicted abundance of CO is too low, by about a factor of 2.5, when compared with the infrared data (Connes et al., 1968). Second, the predicted production rate of H_2SO_4 is too high, about a factor of 3, when compared with the rate inferred from the data of Knollenberg and Hunten (1980). Third, the eddy dffusivity profile needed to produce a sensible solution, while not violating any observations (because none exists), is somewhat artificial. The above weaknesses are not fatal, but uncomfortable. On the other hand, we must recognize that we have made a number of simplifying assumptions in trying to model the atmosphere by a one-dimensional model. The atmosphere of Venus is not homogeneous horizontally (Schloerb et al., 1980; Esposito and Gates, 1981) and agreements to within factors of 2-3 are all that can be demanded of this type of models. To refine the model, we must resort to at least two-dimensional.

Part of the problem lies in the magnitude of L, as given by (25). From (19), we have

$$K \simeq LH^* \qquad (26)$$

Since H^* has been observed to be about 2 km (Winick and Stewart, 1980; Esposito and Gates, 1981), we must choose a high K at the lower boundary to satisfy the SO_2 observations. But a higher K causes rapid transport of CO to the lower atmosphere, thus lowering its abundance above the cloud tops. All three difficulties will be alleviated if L is lower. But this demands a radical revision of the chemistry as listed in Table 3a. This possibility is explored in model C, with a set of reactions given in Table 3c. Unfortunately, as we shall see, a lower value for L aggravates the oxygen problem.

Model B

The chemistry of HSO_3 has recently been investigated and modeled by Davis et al. (1979) and Friend et al. (1980). The authors concluded that the formation of HSO_3 is followed by heterogeneous phase conversion to H_2SO_4 and related acids. Thus the reaction R59

$$SO_2 + OH + M \qquad HSO_3 + M$$

represents a net loss of HO_x. This case is modeled by model A. In model B we examine the possible reactions of HSO_3 with other radicals, O, H, OH, Cl and itself. A simple speculative scheme is given in Table 3b. We argue that the chemical environment in the atmosphere of Venus could be quite different from that on Earth. Specifically, the higher abundance of atomic oxygen could imply

$$k_{66}[O] > k_{67}[H] + k_{68}[OH] + k_{69}[Cl] + k_{70}[HSO_3]$$

and

$$k_{72}[O] > k_{73}[H] + k_{74}[OH] + k_{75}[Cl] + k_{76}[HSO_3]$$

In this case HSO_3 is still oxidized, but the hydroxyl radical is not consumed. The concentrations of HSO_3 and $HSO_3 \cdot H_2O$ predicted by model B are summarized in Figure 15. The important production and loss rates for HSO_3 and $HSO_3 \cdot H_2O$ are given in Figure 16. The concentration of OH is about 60% higher than that in model A, and causes a 30% decrease in the CO concentration at 62 km. Otherwise, the results of model B and A are very similar.

Model C

In this model we want to explore some new chemistry involving the $(SO)_2$ dimer. In the Model A section we discussed the difficulties of model A and indicated a preference for a solution with lower value for the rate of SO_2 oxidation. The $(SO)_2$ chemistry allows for the possibility of a catalytic cycle like cycle (XV), whose net effect is

$$SO + O \qquad SO_2 \ .$$

This is equivalent to increasing k_{50} in (25), and will result in a lower value for L. A speculative chemical scheme with this objective in mind is presented in Table 3c. Inspection of Figure 6c suggests that

$$[(SO)_2] \qquad (27)$$

and $$[S_2O] \qquad (28)$$

Since the RHS of (22) is now completely dominated by the new term R79, we have,

$$J_9[SO_2] \qquad k_{79}[S_2O][O] \tag{29}$$

Solving for [SO] and using (23) and (24), we have,

$$\begin{aligned} L[SO_2] \; = \; & k_{59}[SO_2[O] \\ & J_8[SO] \\ & J_8 \end{aligned} \tag{30}$$

Unfortunately, the key rate coefficient, k_{76}, which determines the stability of the dimer $(SO)_2$ towards thermal decomposition, has not been measured. We assume a somewhat arbitrary value of 1×10^{-23} cm^3 s^{-1}. This results in a much lower rate of SO_2 oxidation. The number densities of O, S, SO, SO_2, S_2O and $(SO)_2$ predicted by model C are shown in Figure 17. The production rates of H_2SO_4, $H_2S_2O_2$, $H_2S_2O_3$ and S_2 are given in Figure 18. A comparison of the major predictions of model A and C is shown in Table 8. The concentration of CO, and the rate of H_2SO_4 production are now in better agreement with the observations, but O_2 is slightly higher. The model allows for modest production rates for thiosulfurous acid, thiosulfuric acid and S_2. It must be emphasized that these results are based on pure speculation.

It is clear that if we were to adjust the rate coefficients of the reactions R80, R81 and R85, we could enormously increase the efficiencies of the schemes (XV), (XVI), and (XVII) for production of H_2SO_4, $H_2S_2O_2$, $H_2S_2O_3$ and S_2. Since these schemes are not limited by oxygen supplied by CO_2 photolysis, the production rates are limited only by SO_2 photolysis rate ~ 1 x 10^{13} cm^{-2} s^{-1}. Such a scenario is unlikely above the cloud tops, though. The CO observation demands a low K at 58 km, and this in turn limits the total loss of SO_2.

Model D

Table 3d summarizes the set of reactions used in model D. The number densities of Cl_2, ClOO, HOCl and COCl are shown in Figure . The computations were performed by holding fixed the number densities of all relevant species computed in model A. Prinn (1971) argued that ClOO could be important as the key species for breaking the O-O bond in cycle (I). Prinn (1972) estimated that the rate coefficient for

$$ClOO + M \qquad Cl + O_2 + M \qquad\qquad (R89)$$

could be as low as 5.2 x 10^{-9} $e^{-4040/T}$. Subsequent measurement suggested that k_{89} = 2.7 x 10^{-9} $e^{-2650/T}$. At ambient temperature in the Venusian stratosphere (~ 250°K) this rate coefficient is 2 orders of magnitude faster than that assumed by Prinn (1972). Hence cycle I becomes totally ineffective.

Krasnopolsky and Parshev (1980a,b) and the present authors argued that COCl could play a role in cycles IVa,b. The present calculations indicate that COCl does not play any significant role in breaking the O-O bond. The reason for the difference between our conclusion and that of Krasnopolsky and Parshev (1980a,b) is that we have 5 orders of magnitude more H_2 in our model (see Table 7) and we have used a higher value for the rate coefficient for R93,

$$COCl + M \qquad CO + Cl + M ,$$

on the basis of our own experiments.

The altitude profiles for the odd nitrogen species, N, NO, NO_2, NO_3, HNO_2 and HNO_3 are given in Figure 20. In the NO_x calculations, the concentrations of all species computed in model A are held fixed. The only source of NO_x is a downward flux of atomic nitrogen equal to 1 x 10^{10} atoms cm^{-2} s^{-1} at the upper boundary at 110 km. Most of odd nitrogen is destroyed in the upper stratosphere by R111,

$$N + NO \qquad N_2 + O .$$

The rest of the odd nitrogen is lost to the lower atmosphere as NO. We have not included any source of NO_x due to lightning (Watson et al., 1979), because there is probably no lightning in the stratosphere, and it is unlikely that NO_x produced in the lower atmosphere can diffuse upward to the cloud tops. Using the concentrations of NO_x species given in Figure 20, it can be shown that R109,

$$NO + ClO \qquad NO_2 + Cl ,$$

is not important, when compared with R55; and that R112,

$$NO_2 + O \qquad NO + O_2 ,$$

is not an important sink for odd oxygen.

Miscellaneous Topics

Molecular hydrogen

Our photochemical modeling supports the high concentration of H_2 recently inferred by Kumar et al. (1981). The presence of order of 10 ppm is needed to drive the OH mediated CO_2 recombination catalytic cycles, and for suppressing the chlorine cycle that leads to production of O_2. It remains a challenging problem to understand why the Venusian atmosphere has so much H_2. Direct photochemical production of H_2 above the cloud tops is negligible. The only known reservoirs of hydrogen species in the stratosphere is HCl and H_2O. Photochemical destruction of H_2O is exceedingly slow due to nearly complete shielding of ultraviolet radiation by CO_2. Conversion of HCl into H_2 in models A and C is small. But even if complete conversion of HCl were possible, this would yield only 0.2 ppm H_2.

Thermochemical equilibrium in the lower atmosphere yields the following relations between H_2, H_2O, H_2S, CO, CO_2 and COS:

The equilibrium constants K_1, K_2 and K_3 have been evaluated using data presented in the JANAF Thermochemical Tables (1971). Note that $K_1 = K_2K_3$. These equilibrium relations reveal that H_2O and H_2S could provide a source of H_2 at least in principle. However, in the regions of the atmosphere where equilibrum can be rapidly established, the predicted H_2 is of order of 3×10^{-9}. Hence it is unlikely that thermochemical equilibrium chemistry can maintain a concentration of H_2 of order 10 ppm in the lower atmosphere. On the contrary, the lower atmosphere near the surface may be an important sink for H_2, converting H_2 into H_2O, which is more stable thermodynamically.

As pointed out by Kumar et al. (1981), the production of H_2 in the lower atmosphere probably involves disequilibrium chemistry, driven perhaps by absorption of near ultraviolet or visible radiation by sulfur polymers (Prinn, 1978, 1979). There has been no theoretical or experimental study on the production of polysulfur from SO_2. On the basis of the reaction,

$$S + O_2 \qquad SO + O \qquad\qquad (R46)\ ,$$

Winick and Stewart (1980) argued that generation of polysulfur photochemically is not possible. We have extended the work of Winick and Stewart (1980), and presented, in model C, the possibility of making a variety of disequilibrium sulfur compounds: S_2, S_2O, $(SO)_2$, $H_2S_2O_2$ and $H_2S_2O_3$. In all previous photochemical studies of Venus the arrow of oxidation was assumed to have one direction for sulfur compounds, such as from COS to H_2SO_4 (Prinn, 1973, 1975) and SO_2 to H_2SO_4 (Winick and Stewart, 1980). In this work (model C) we first raise the possibility of the segregation of this chemical system into more reduced and a more oxidized compounds simultaneously by the schemes XV - XVIII. The photochemical production and downward transport of this set of highly reduced disequilibrium products may have profound implications for the chemistry of the lower atmosphere. However, the lack of sufficient laboratory data does not permit us presently to evaluate the consequences of model C.

Comparison with Earth's stratosphere

In recent years, considerable effort has been directed to understand the processes that control the abundance of ozone in the Earth's stratosphere, and to assess the impact of perturbations by supersonic transport (SST) aviation (Crutzen, 1970; Johnston, 1971; McElroy et al., 1974), the release of chlorofluoromethanes (Molina and Rowland, 1974; McElroy et al., 1974; Cicerone et al., 1974; Wofsy et al., 1975; NAS 1976; NASA, 1977, 1979; Crutzen et al., 1978), and the release of N_2O associated with the use of fertilizers in agriculture (McElroy et al., 1977; Logan et al., 1978). The chemistry of the stratosphere of Venus offers a valuable system for testing and extending our knowledge of the chemistry of the Earth's stratosphere. In fact, historically, the chlorine chemistry of Venus was developed before the importance of chlorine chemistry in the Earth's atmosphere was recognized (Prinn, 1971; McElroy et al., 1973).

Table 9 summarizes a comparison of some essential aspects of stratospheric chemistry on the two planets. The ambient pressures and temperatures are comparable. The abundances of chlorine and sulfur species on Venus are about 200 and 500 times, respectively, larger than those on Earth. The Molina-Rowland chlorine cycle for catalytic conversion of odd oxygen into molecular oxygen is eminently important for both planets. In the Earth's stratosphere, the effectiveness of the chlorine cycle is suppressed by the reaction,

$$\mathrm{Cl + CH_4 \qquad HCl + CH_3}\ ,$$

which turns an active chlorine radical into a relatively inert form as HCl. On Venus, reaction R38,

$$\mathrm{Cl + H_2 \qquad HCl + H}\ ,$$

plays a similar role. Indeed, if the chlorine cycle were allowed to operate unchecked, the amount of O_2 produced could easily violate the observed upper limit, as in Winick and Stewart (1980).

Logan et al. (1978) pointed out that there is a synergistic effect between ozone perturbations by chlorine and odd nitrogen, such that the impact of the Molina-Rowland cycle is mitigated. The crucial reaction is

$$\mathrm{ClO + NO \qquad Cl + NO_2}\ , \qquad \text{(R110)}$$

which leads to a net nothing cycle and competes with the reaction that destroys odd oxygen,

$$\mathrm{ClO + O \qquad Cl + O_2}\ . \qquad \text{(R44)}$$

On Venus, NO_x is more deficient. Instead, the reaction

$$ClO + SO \qquad Cl + SO_2 \qquad\qquad (R55)$$

plays a similar role as (R110) and amounts to as much as 25% of R44.

Removal of active radicals, such as OH, Cl and H_2O_2 by heterogeneous processes in the Earth's stratosphere is a subject of great interest, since such losses could reduce the impact of chlorofluorocarbons on ozone. The current understanding is that heterogeneous processes are not important (Baldwin and Golden, 1979; NASA, 1979), except perhaps during periods of enhanced volcanic activity (Stratton et al., 1979). However, in the stratosphere of Venus, SO_2 is much more abundant and provides an important heterogeneous sink for OH and Cl in our models A and C. Unfortunately, the kinetics of heterogeneous chemistry of sulfur compounds is not sufficiently well understood to firmly establish the importance of this possibility.

In the assessment of the impact of SST aviation on the ozone layer (McElroy et al., 1974), a major revision of the conclusions had to be made on account of reaction R109 (Howard and Evenson, 1977),

$$NO + HO_2 \qquad NO_2 + OH$$

which destroys odd oxygen. On Venus, the analog of R109 is R49,

$$SO + HO_2 \qquad SO_2 + OH \, .$$

Reaction R49, together with R46,

$$S + O_2 \qquad SO + O \, ,$$

are extremely important for breaking up and using molecular oxygen for SO_2 oxidation. Although the rate coefficient k_{49} has not been measured, we believe that our estimate, as given in Table 3a, must be good to within a factor of 2.

Broad-band UV absorber

In the extensive study on the distribution and source of ultraviolet absorption in the Venusian atmosphere, Pollack et al. (1980) concluded that the absorption from 0.2 to 0.32 could be adequately accounted for by SO_2, but the identity of the absorber for the region 0.32 to 0.40 is uncertain. Pollack et al's tentative suggestion of gaseous Cl_2 as a possible candidate is incompatible with our modeling results (see section Model D). In our photochemical model (Model C), we explore the chemistry of a number of interesting sulfur compounds: S_2, S_2O, $(SO)_2$, $H_2S_2O_2$ and $H_2S_2O_3$. It is conceivable that some of these compounds may explain the observed UV absorption longward of 0.32 . Experiments on the optical properties of S_2, $(SO)_2$, $H_2S_2O_2$ and $H_2S_2O_3$ must be done to assess this possibility.

Conclusions

We have presented chemical models of the stratosphere of Venus that can satisfactorily account for the observations. In the upper stratosphere ($\gtrsim$ 70 km) CO_2 recombination is mediated by cycle II. The reaction R25, CO + OH, plays a crucial role, with the hydroxyl radical supplied by HCl photolysis. The oxygen atoms that are not consumed by CO recombine to form O_2 via R17, O + O + M, R28, O + OH and R44, ClO + O. The reactions R17, R31 O + HO_2, and R44 may provide major sources of $O_2(^1\ )$ emission at 1.27 . Molecular oxygen that is transported downward to the lower stratosphere (~ 58-70 km) can be used to oxidize SO_2 to H_2SO_4 by the schemes Va,b and XII. The crucial reactions that break the O-O bond are R46, S + O_2 and R54, SO + HO_2. The presence of a high H_2 concentration (~ 10 ppm) is preferred by our models.

There remain a number of uncertainties in the models that could be removed by suitable observations and laboratory experiments. A recommended list is summarized in Table 10. The species O_2, SO and H_2 occupy a central position in our chemical schemes. They have not been directly detected by spectroscopic observations. The quantum yields for producing $O_2(^1\ )$ in reactions R17 and R44 have not been measured. The rate coefficient for the O-O bond breaking reaction R54 has not been measured. In addition, the chemistry of $(SO)_2$ dimer, which could lead to the formation of interesting compounds such as S_2, $H_2S_2O_2$ and $H_2S_2O_3$, is almost totally unknown.

The distribution of major chemical species in the stratosphere has been observed to be inhomogeneous horizontally. The one-dimensional photochemical model is a crude approximation and can only reproduce the observations to within factors of 2-3. To realistically model the stratosphere, and to study the latitudinal and longitudinal variation, we must resort to at least a two-dimensional model. Observations of the global distributions of CO, SO_2,, O, O_2 and H_2SO_4 aerosols are needed.

The chemistry of the stratosphere of Venus bears interesting similarities to that of the Earth. On both planets, the classic Molina-Rowland cycle for catalytic conversion of odd oxygen into molecular oxygen (cycle VIII) is important. In the terrestrial stratosphere, the efficiency of cycle (VIII) is inhibited by $Cl + CH_4$ and $ClO + NO$. These inhibiting reactions have almost exact analogs in the Venusian stratosphere in R38, $C + H_2$ and R55, $ClO + SO$. Heterogeneous removal of HO_x and ClO_x radicals by SO_2 is most likely to be important on Venus, whereas similar processes are probably not important in the terrestrial stratosphere. The reaction $NO + NO_2$, which is critical for the assessment of the impact of SST and fertilizer on the ozone layer in the terrestrial stratosphere, has a Venusian analog in the reaction R54 $SO + HO_2$. In view of such obvious similarities between the chemistry of the stratospheres of Venus and the Earth, comparative studies of both planets will be fruitful.

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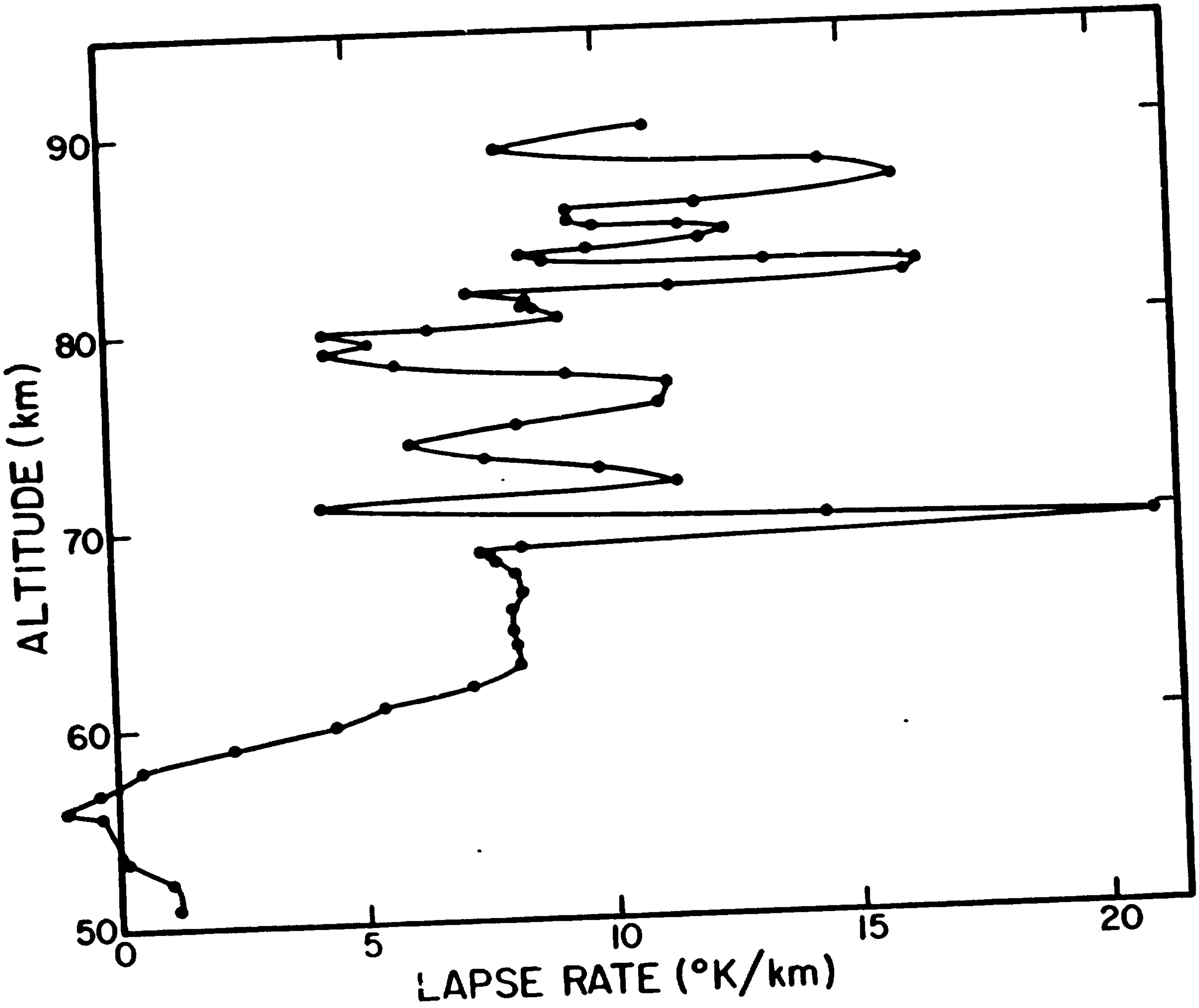
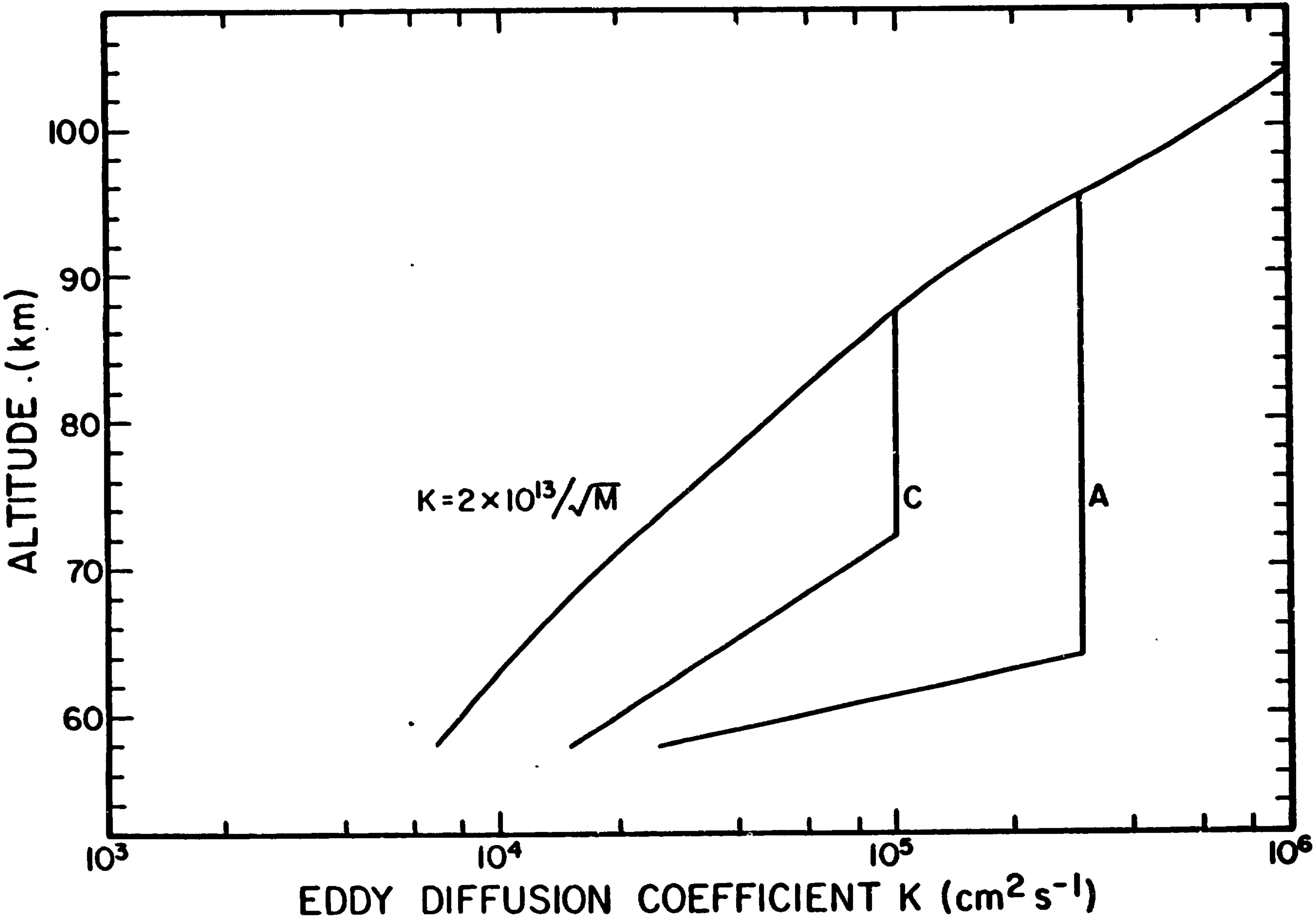
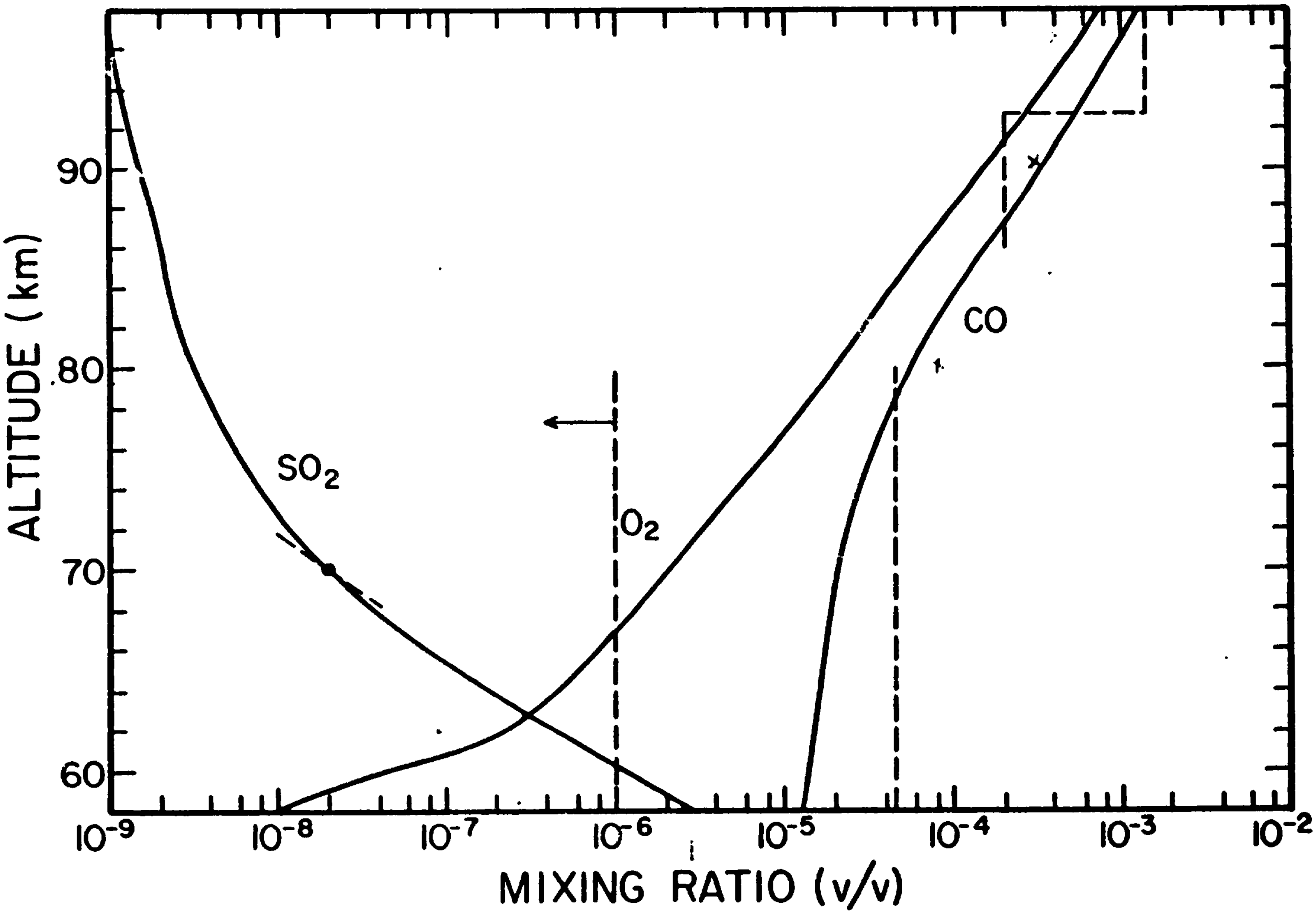
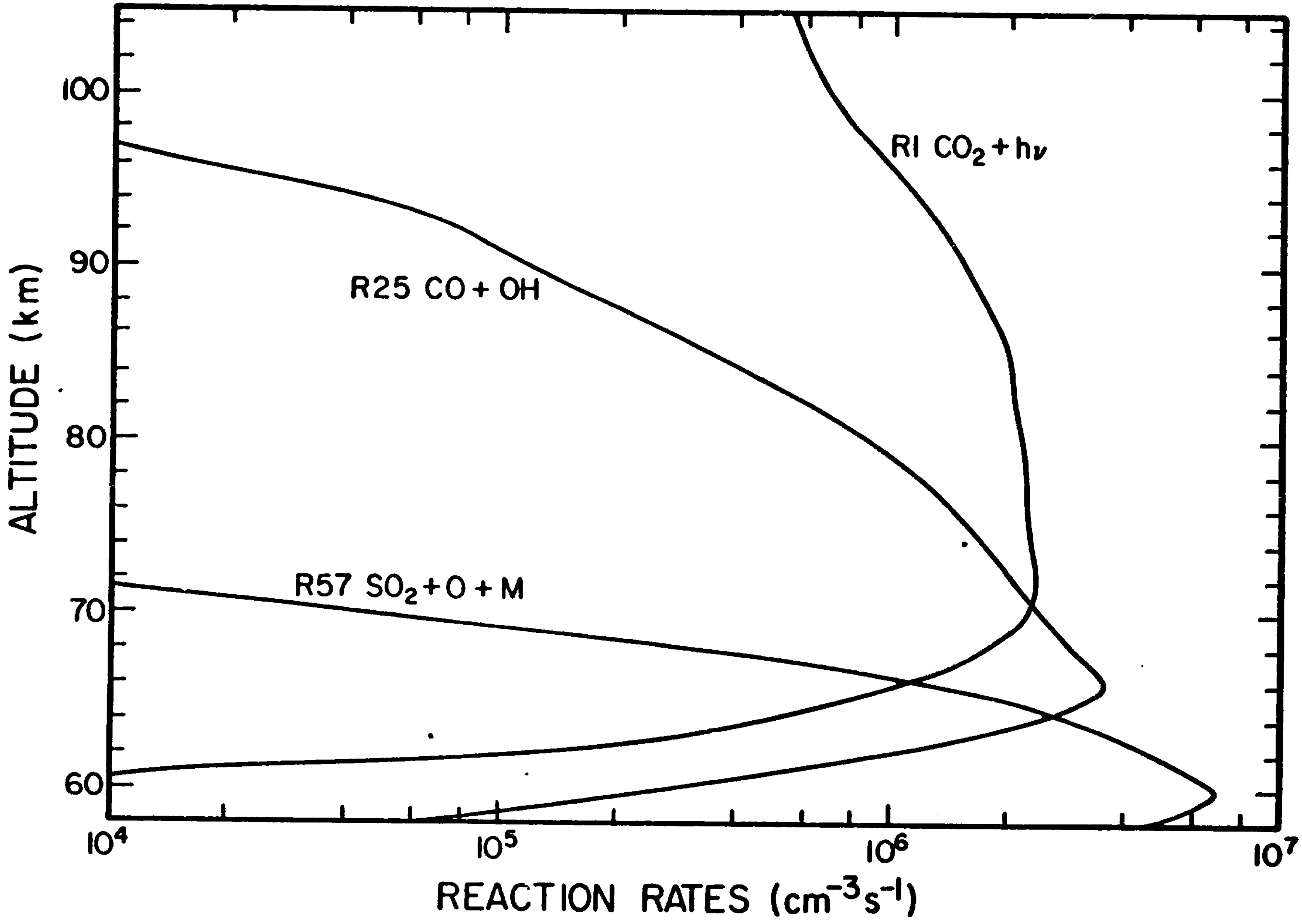
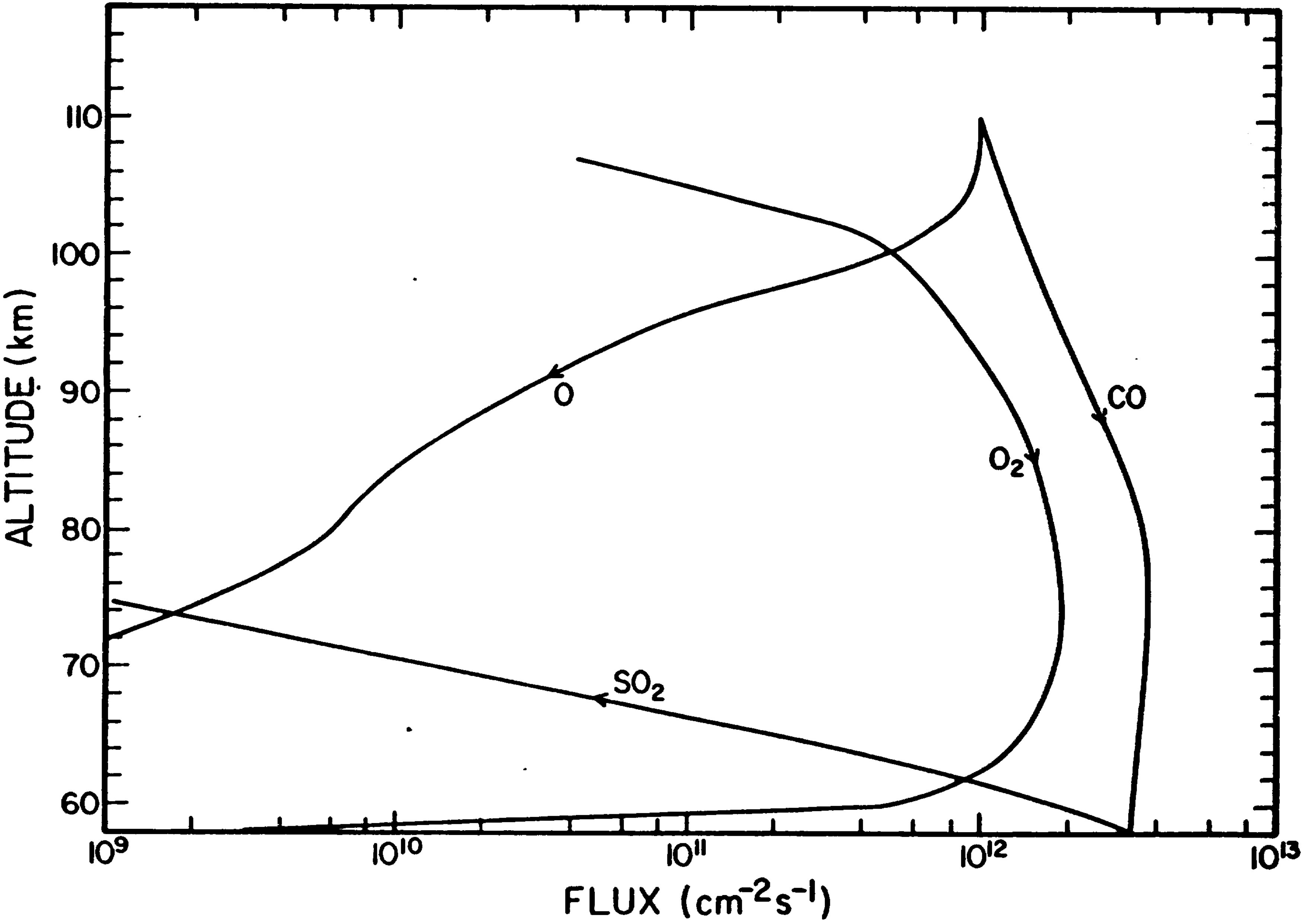

ALTITUDE (km)
90
80
70
60
50
LAPSE RATE (°K/km)
0
5
10
15
20

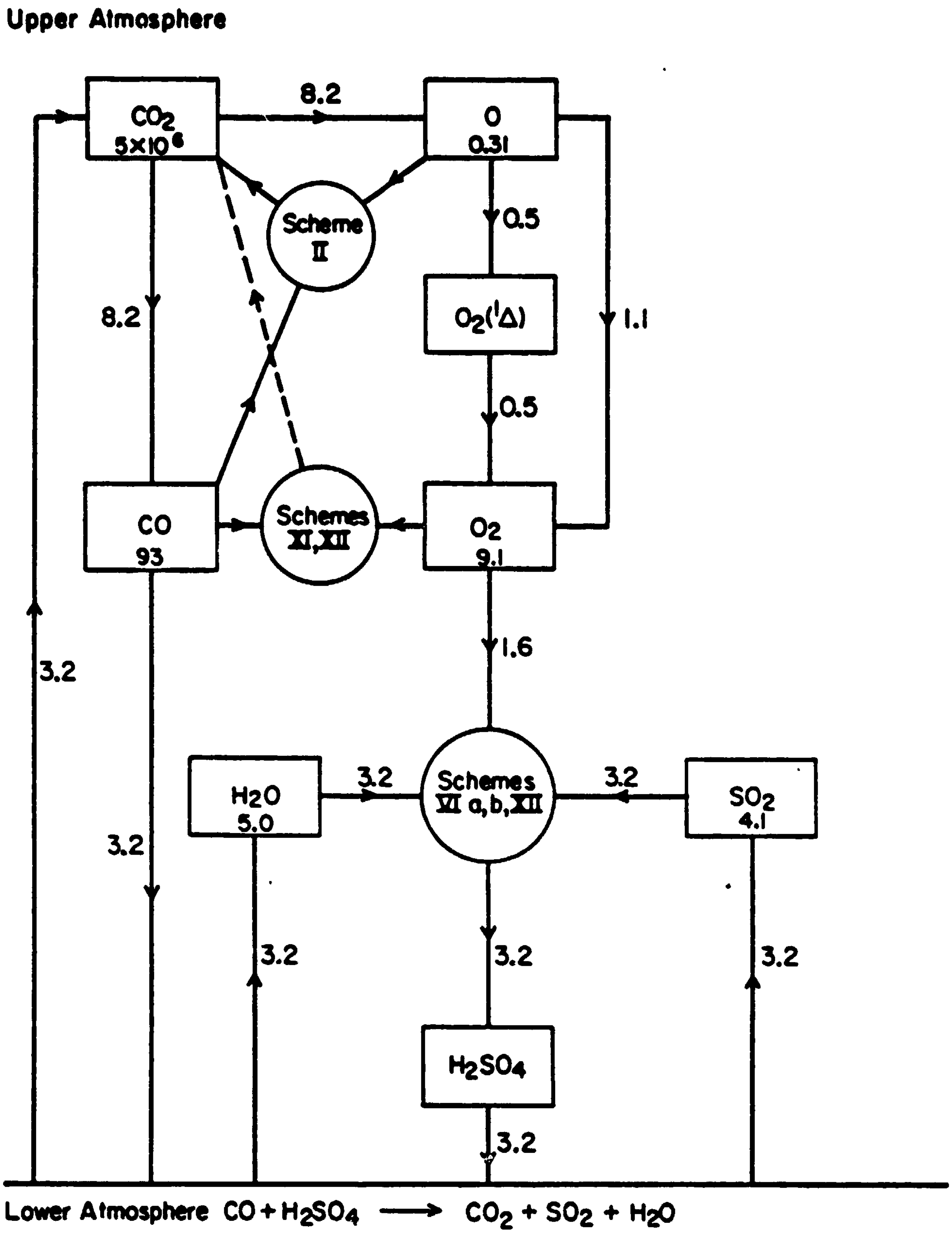

ALTITUDE .(km)
100
90
80
70
60
10^3
10^4
10^5
10^6
EDDY DIFFUSION COEFFICIENT K (cm^2 s^-1)
K=2×10^13/√M
C
A

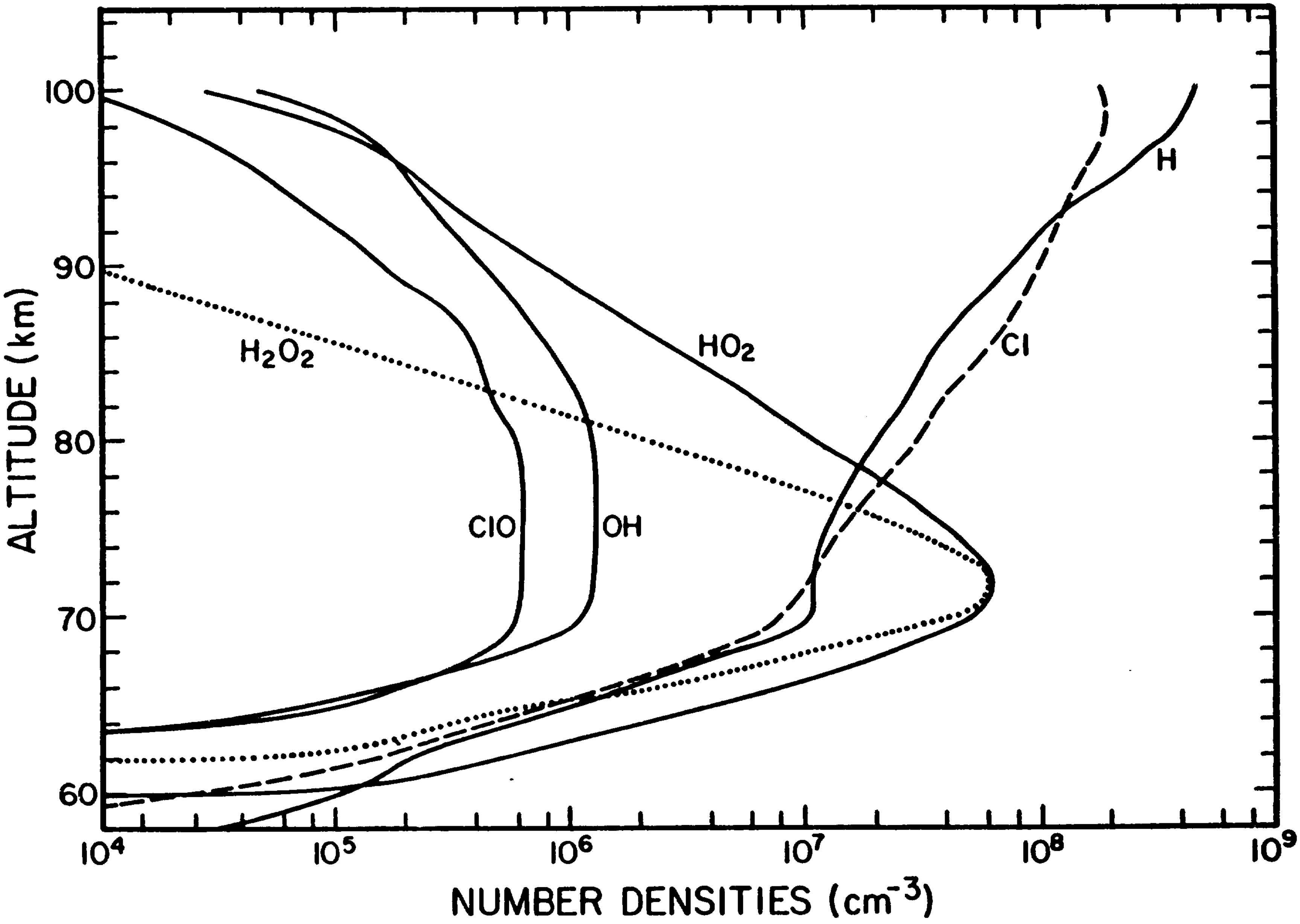

ALTITUDE (km)
90
80
70
60
MIXING RATIO (v/v)
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
SO_2
O_2
CO

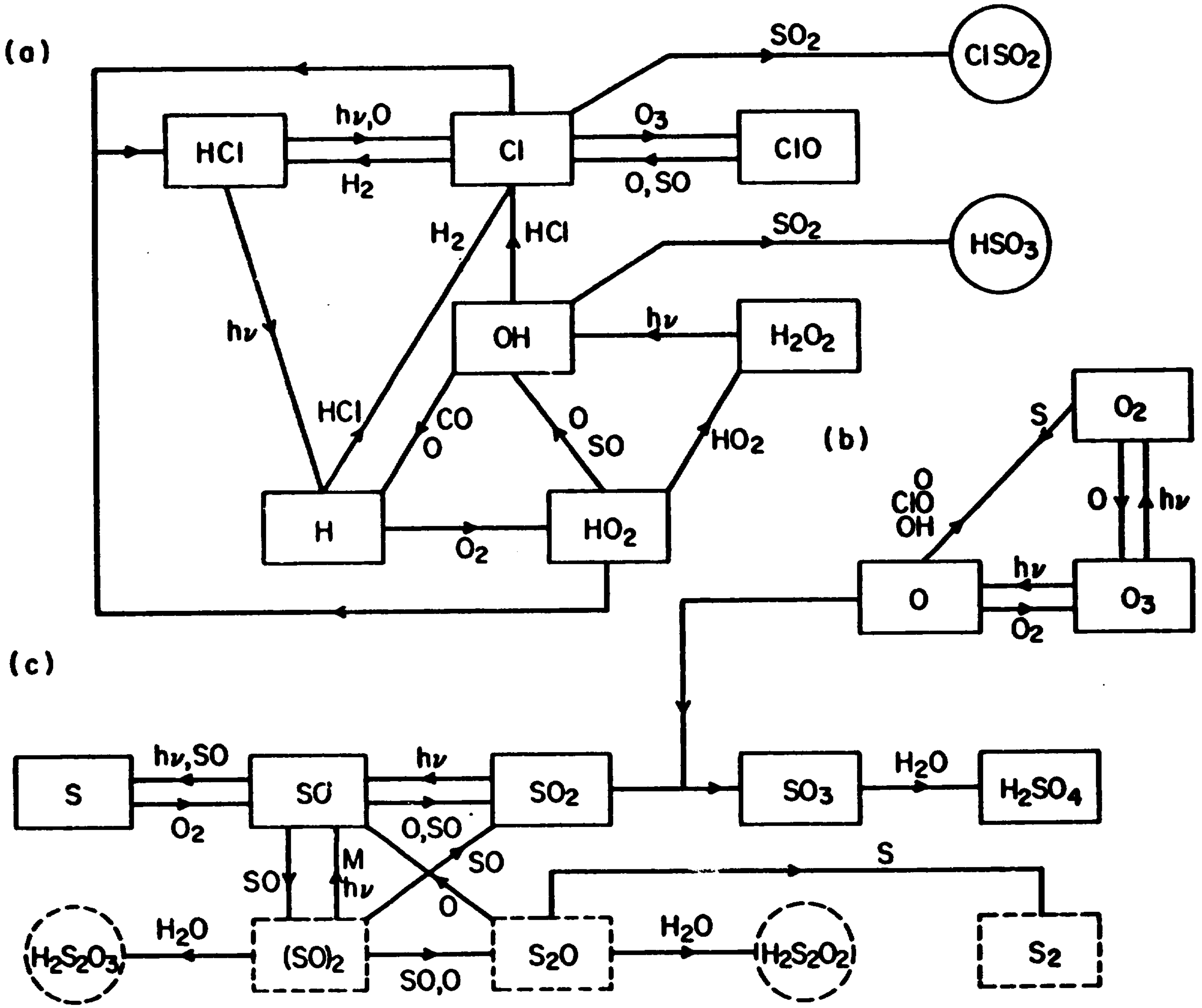
2

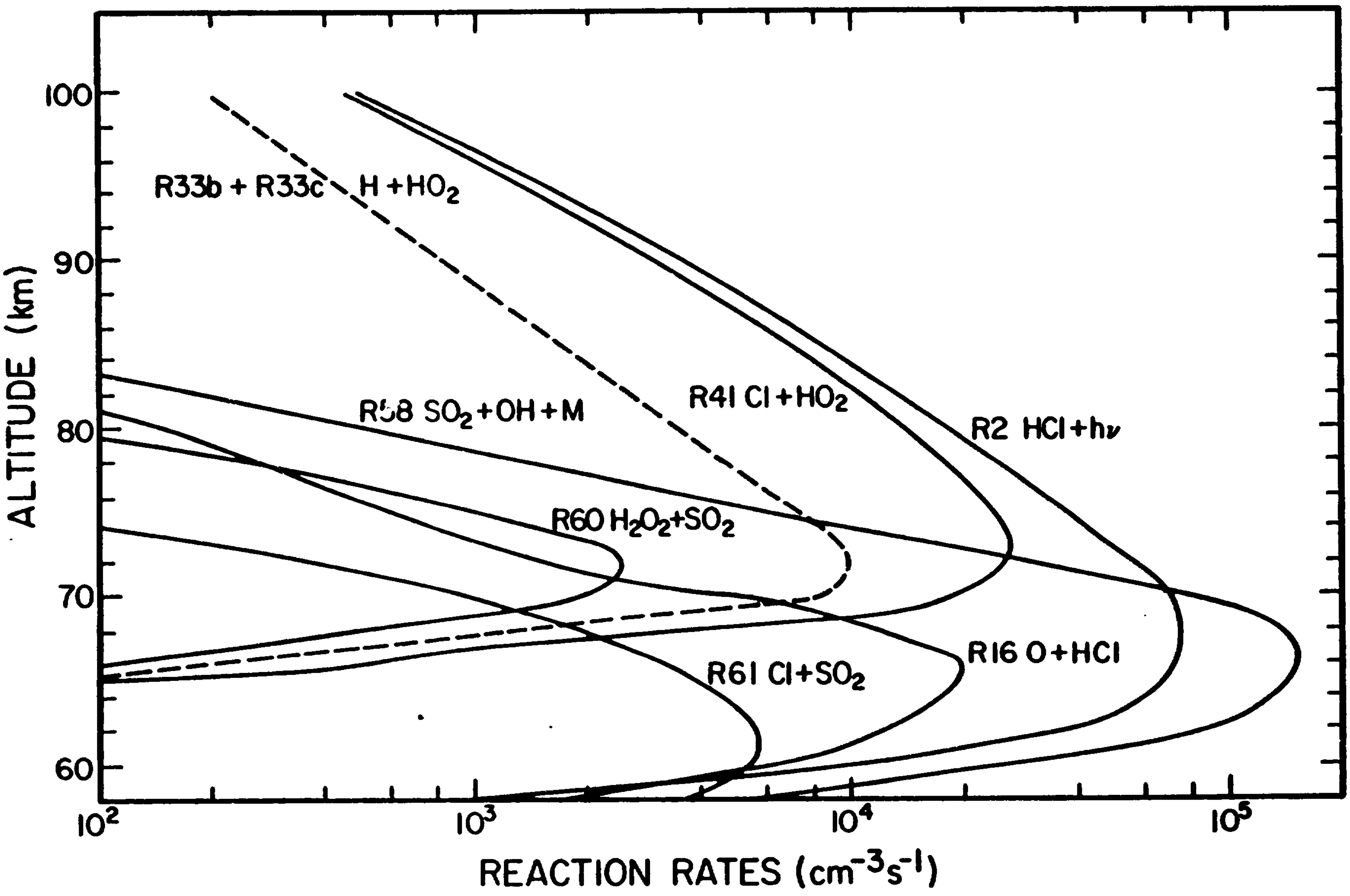

ALTITUDE (km)
100
90
80
70
60
R1 $CO_2 + h\nu$
R25 CO + OH
R57 $SO_2 + O + M$
10^4
10^5
10^6
10^7
REACTION RATES ($cm^{-3}s^{-1}$)

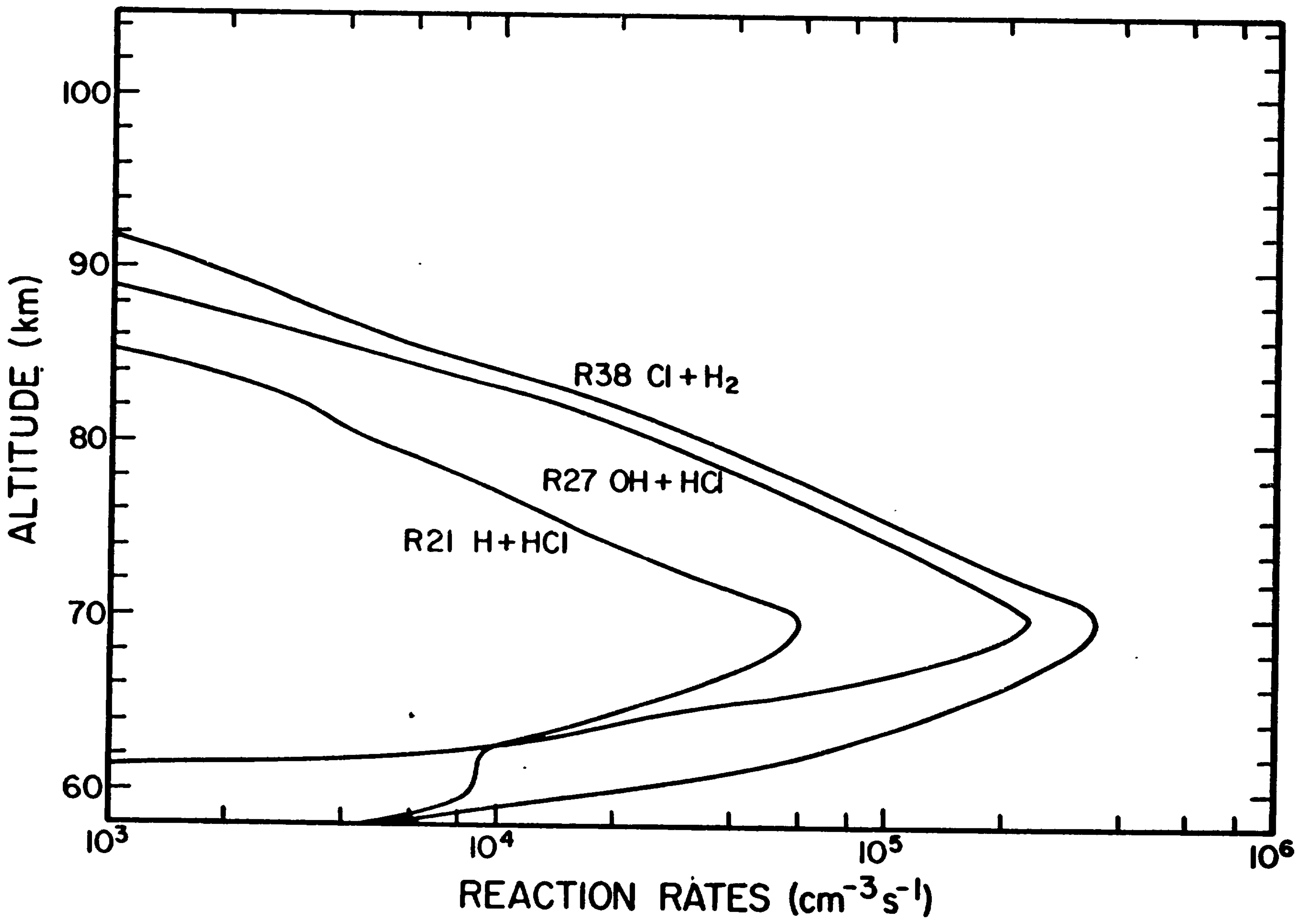

ALTITUDE (km)
110
100
90
80
70
60
10^9
10^{10}
10^{11}
10^{12}
10^{13}
FLUX ($cm^{-2}s^{-1}$)
O
CO
O_2
SO_2


Upper Atmosphere
CO2 5×10^6
8.2
O 0.31
Scheme II
0.5
O2(1Δ)
8.2
1.1
0.5
CO 93
Schemes XI, XII
O2 9.1
1.6
3.2
H2O 5.0
3.2
Schemes VI a, b, XII
3.2
SO2 4.1
3.2
3.2
3.2
3.2
H2SO4
3.2
Lower Atmosphere CO + H2SO4 ⟶ CO2 + SO2 + H2O

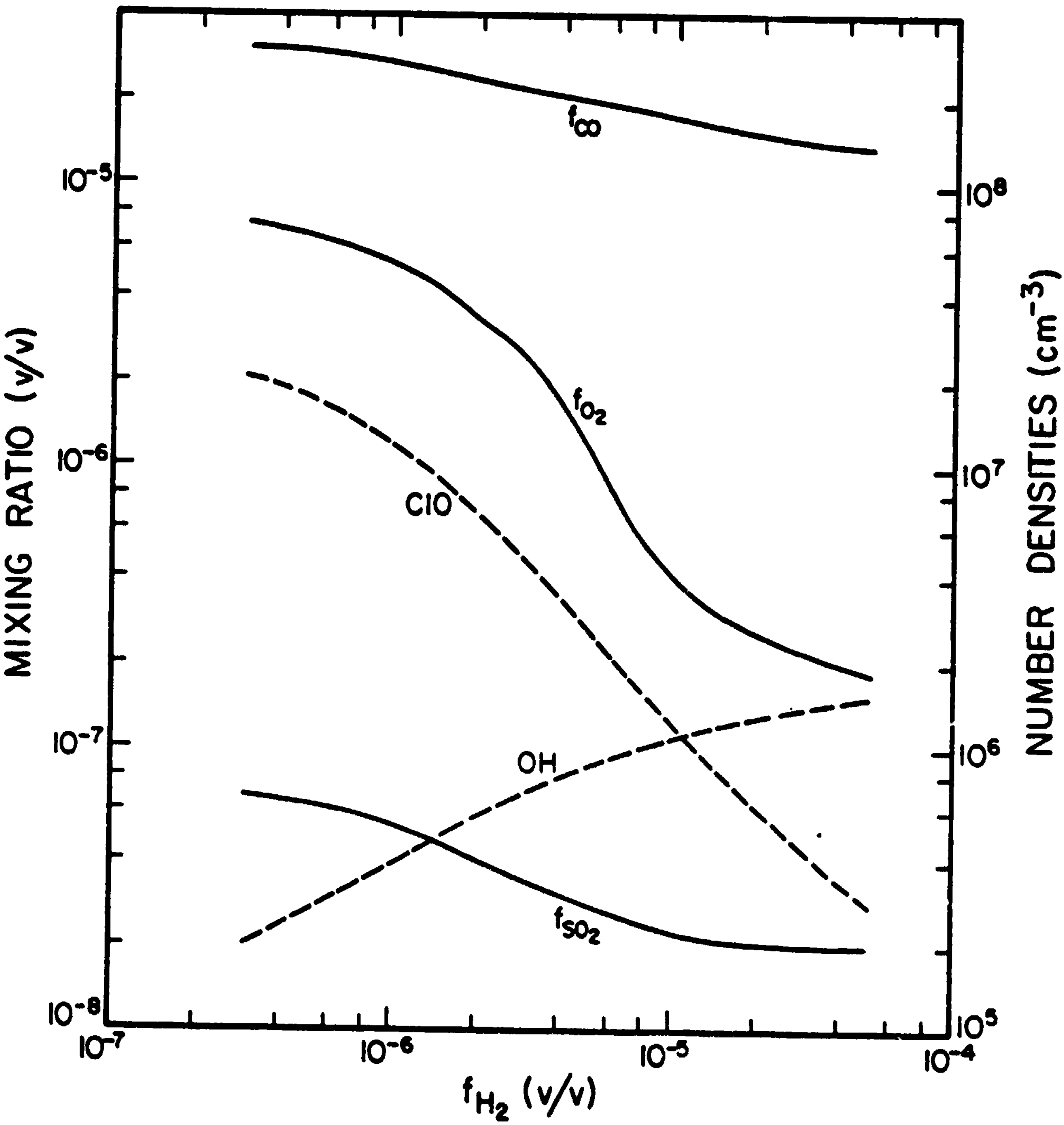

ALTITUDE (km)
100
90
80
70
60
NUMBER DENSITIES (cm^{-3})
10^4
10^5
10^6
10^7
10^8
10^9
H
Cl
HO_2
H_2O_2
ClO
OH


(a)
(b)
(c)
HCl
Cl
ClO
ClSO2
HSO3
OH
H2O2
H
HO2
hν,O
H2
O3
O, SO
SO2
SO2
H2
HCl
hν
hν
HCl
CO
O
O
SO
HO2
O2
O2
O3
O
S
O
ClO
OH
O
hν
hν
O2
S
SO
SO2
SO3
H2SO4
hν,SO
O2
hν
O,SO
H2O
SO
M
hν
SO
O
S
H2S2O3
(SO)2
S2O
H2S2O2
S2
H2O
SO,O
H2O

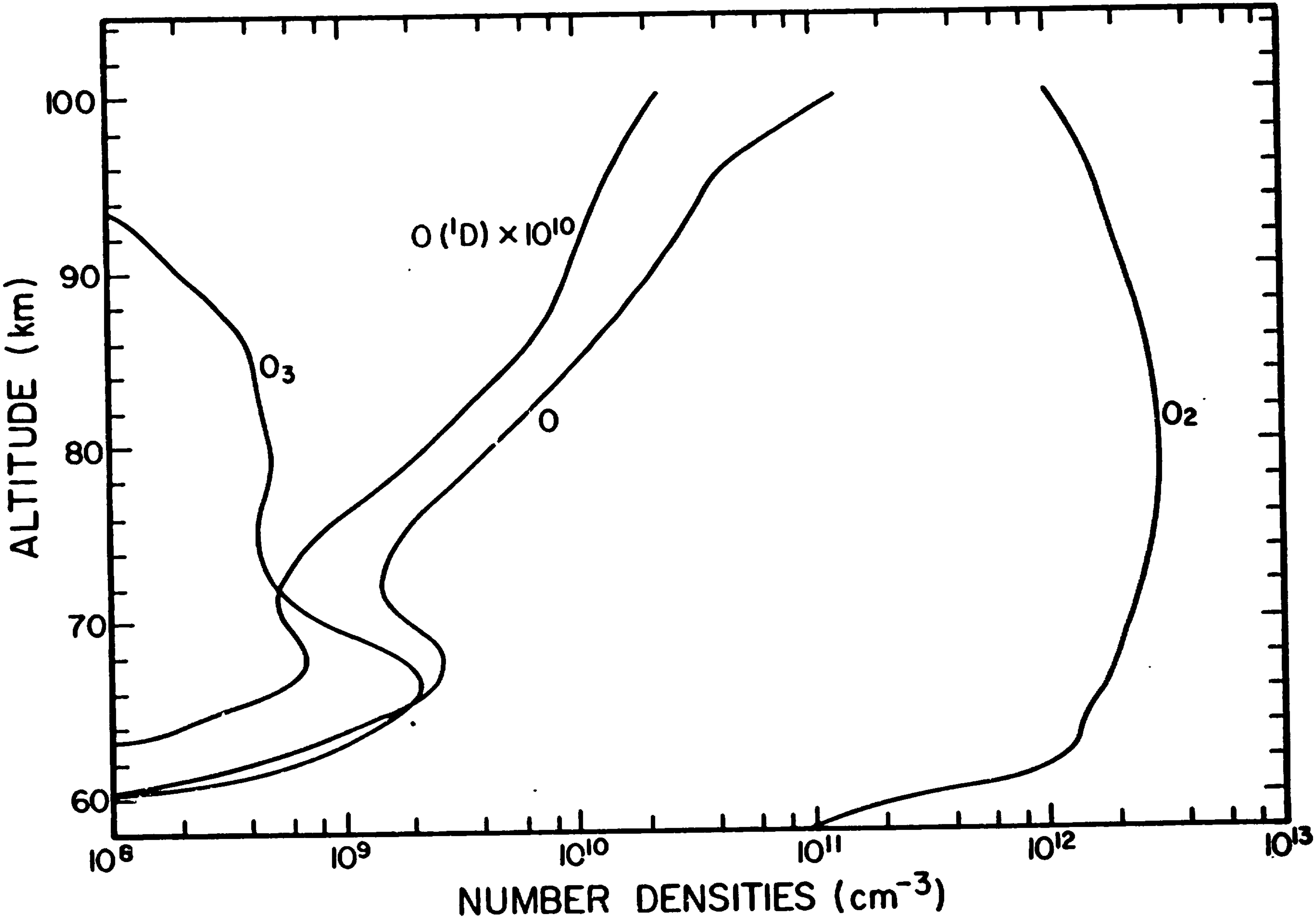

R33b + R33c H + HO_2
R41 Cl + HO_2
R2 HCl + hν
R58 SO_2 + OH + M
R60 H_2O_2 + SO_2
R16 O + HCl
R61 Cl + SO_2
ALTITUDE (km)
100
90
80
70
60
10^2
10^3
10^4
10^5
REACTION RATES ($cm^{-3}s^{-1}$)

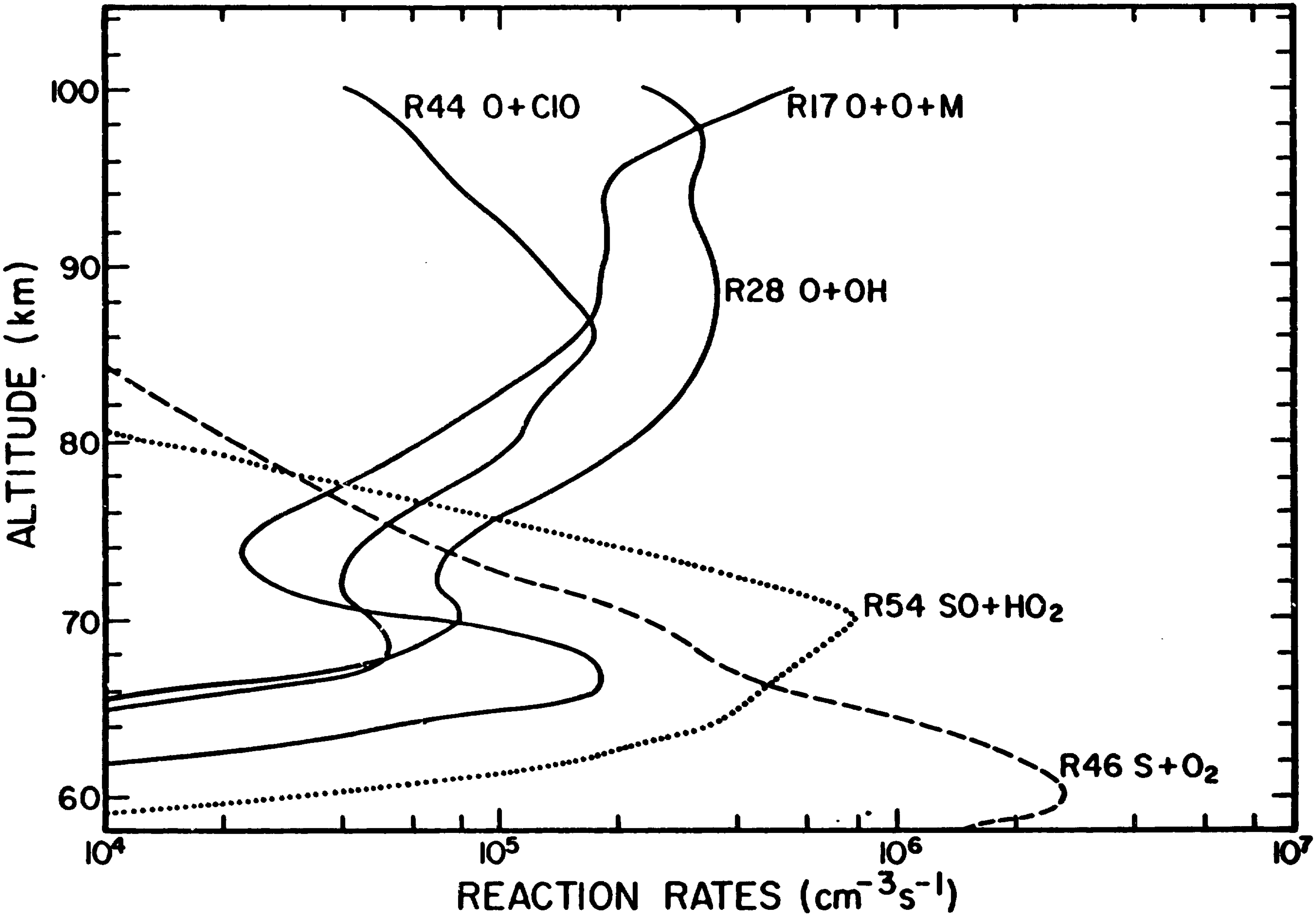


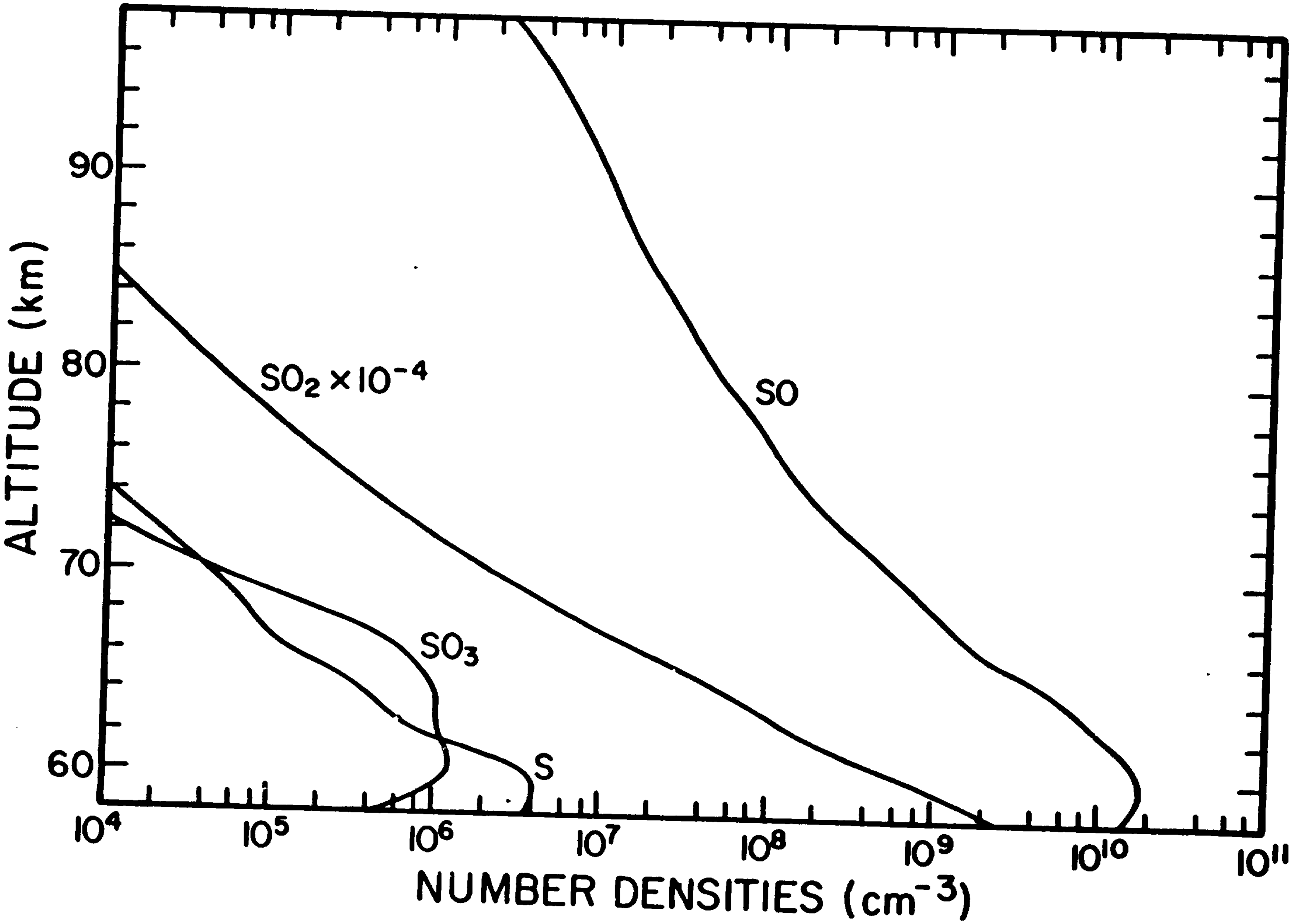
ALTITUDE (km)
100
90
80
70
60
R38 Cl + H_2
R27 OH + HCl
R21 H + HCl
10^3
10^4
10^5
10^6
REACTION RATES ($cm^{-3}s^{-1}$)

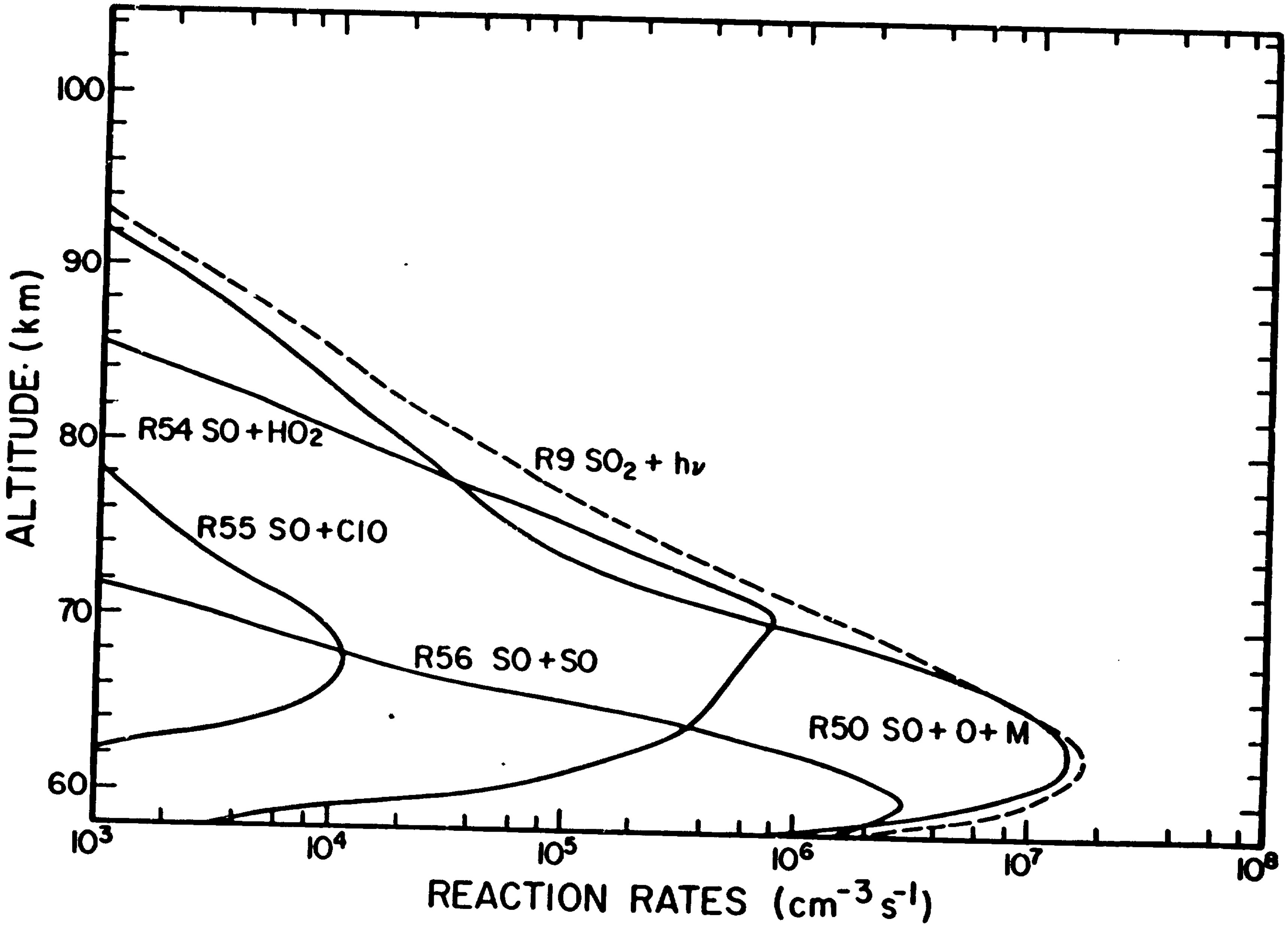


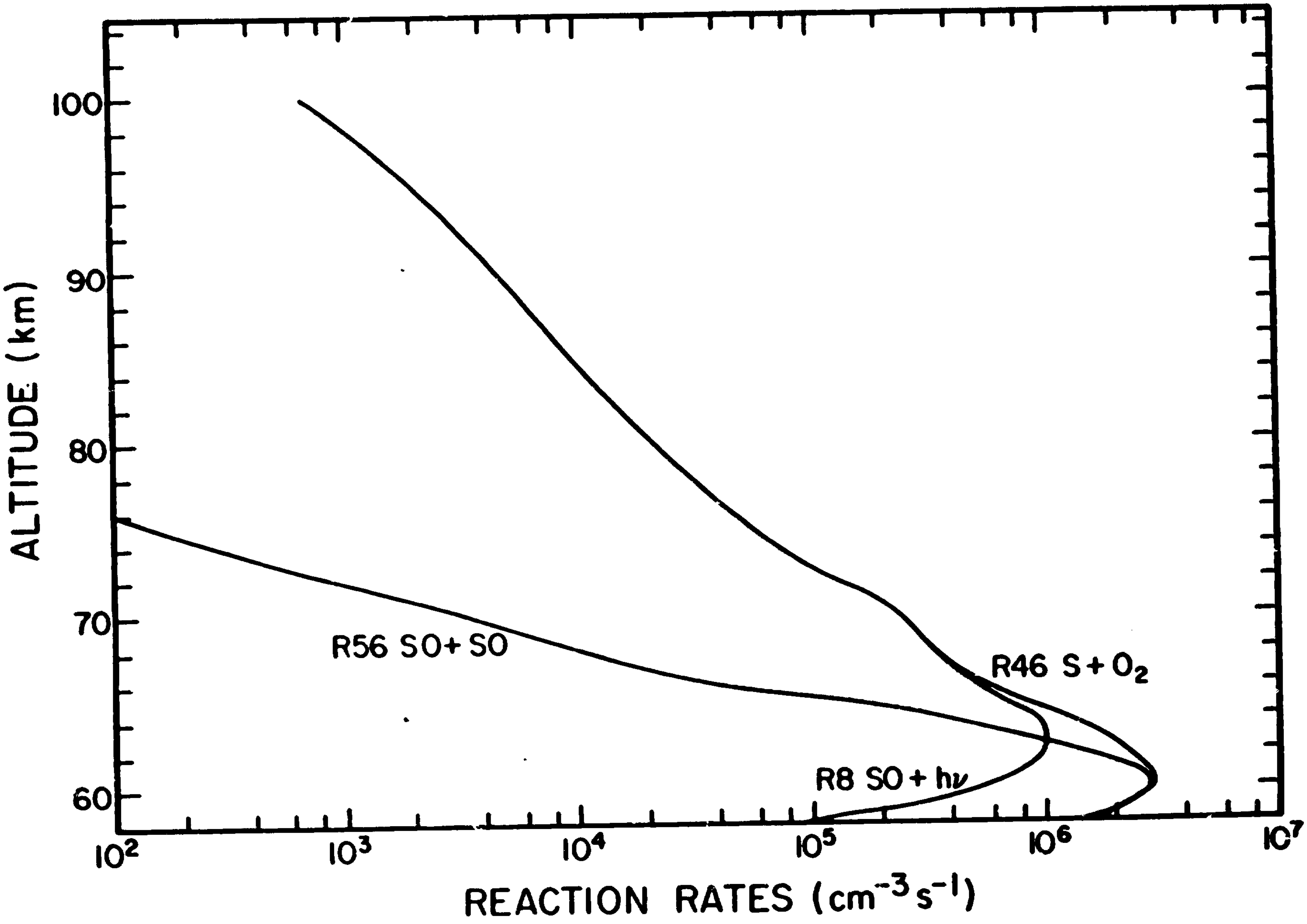
MIXING RATIO (v/v)
NUMBER DENSITIES (cm^{-3})
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{8}
10^{7}
10^{6}
10^{5}
f_{CO}
f_{O_2}
ClO
OH
f_{SO_2}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
f_{H_2} (v/v)

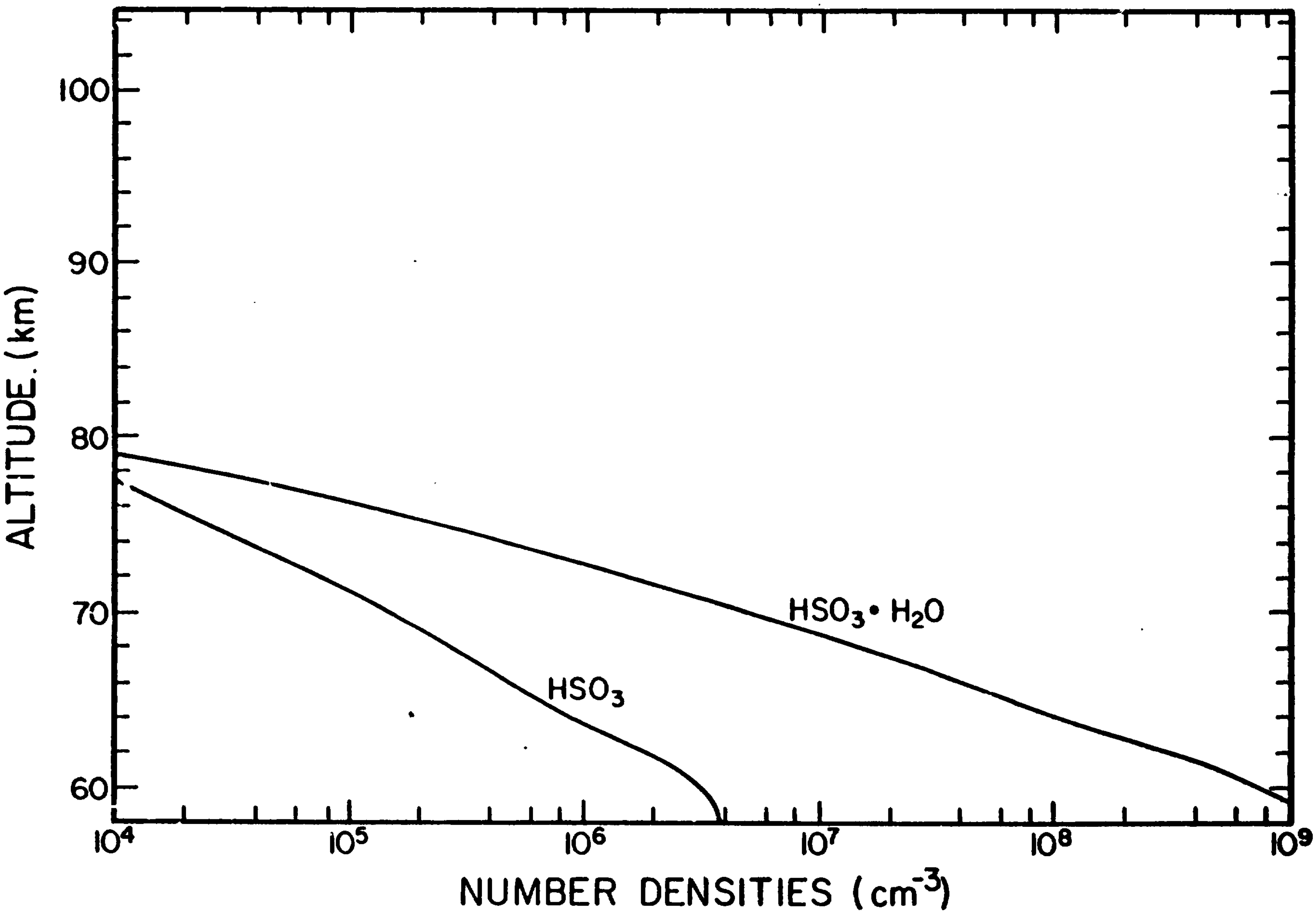

ALTITUDE (km)
100
90
80
70
60
NUMBER DENSITIES (cm^{-3})
10^8
10^9
10^{10}
10^{11}
10^{12}
10^{13}
O_3
O (^{1}D) × 10^{10}
O
O_2

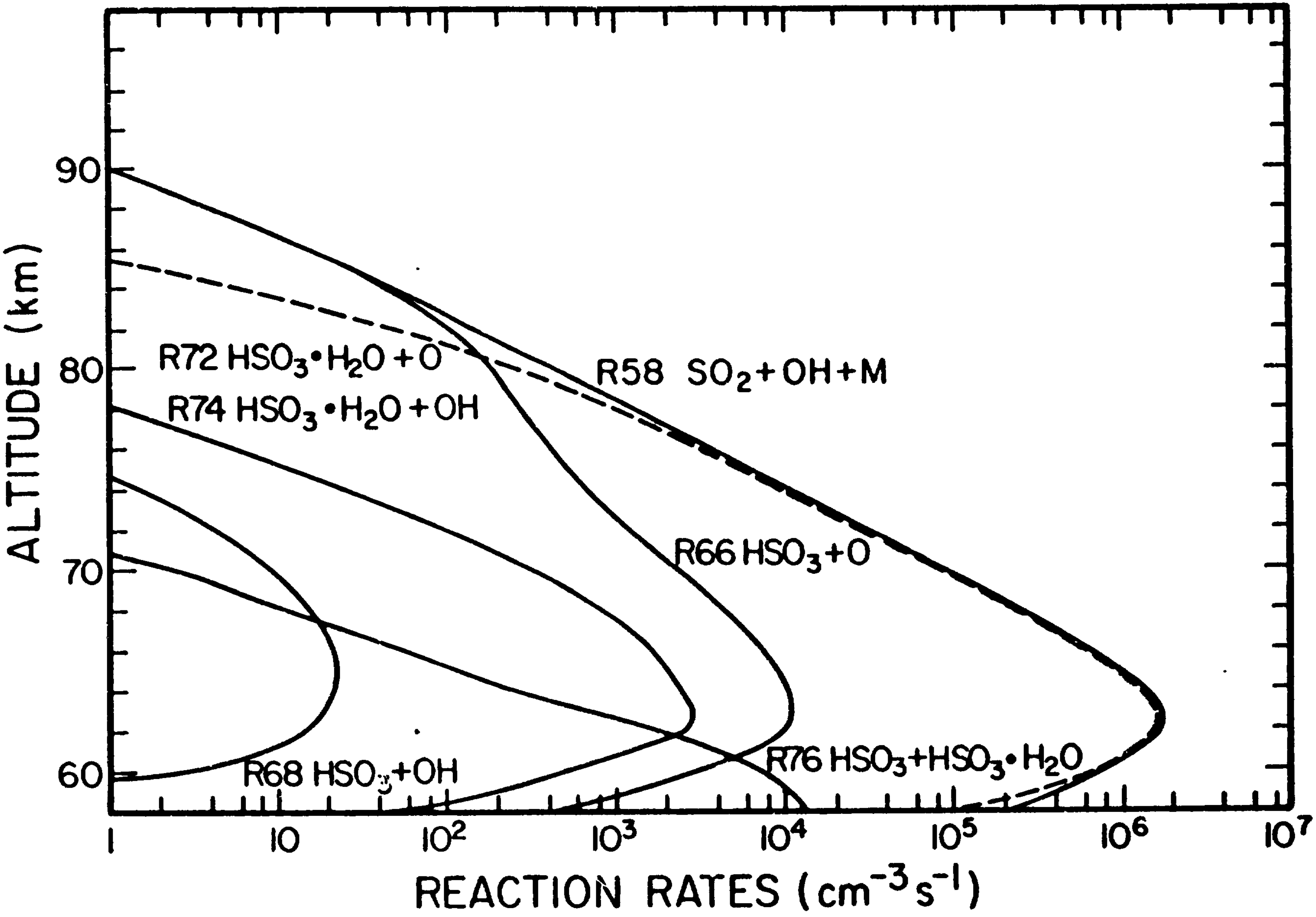

R44 O+ClO
R17 O+O+M
R28 O+OH
R54 SO+HO₂
R46 S+O₂
ALTITUDE (km)
100
90
80
70
60
10⁴
10⁵
10⁶
10⁷
REACTION RATES (cm⁻³s⁻¹)

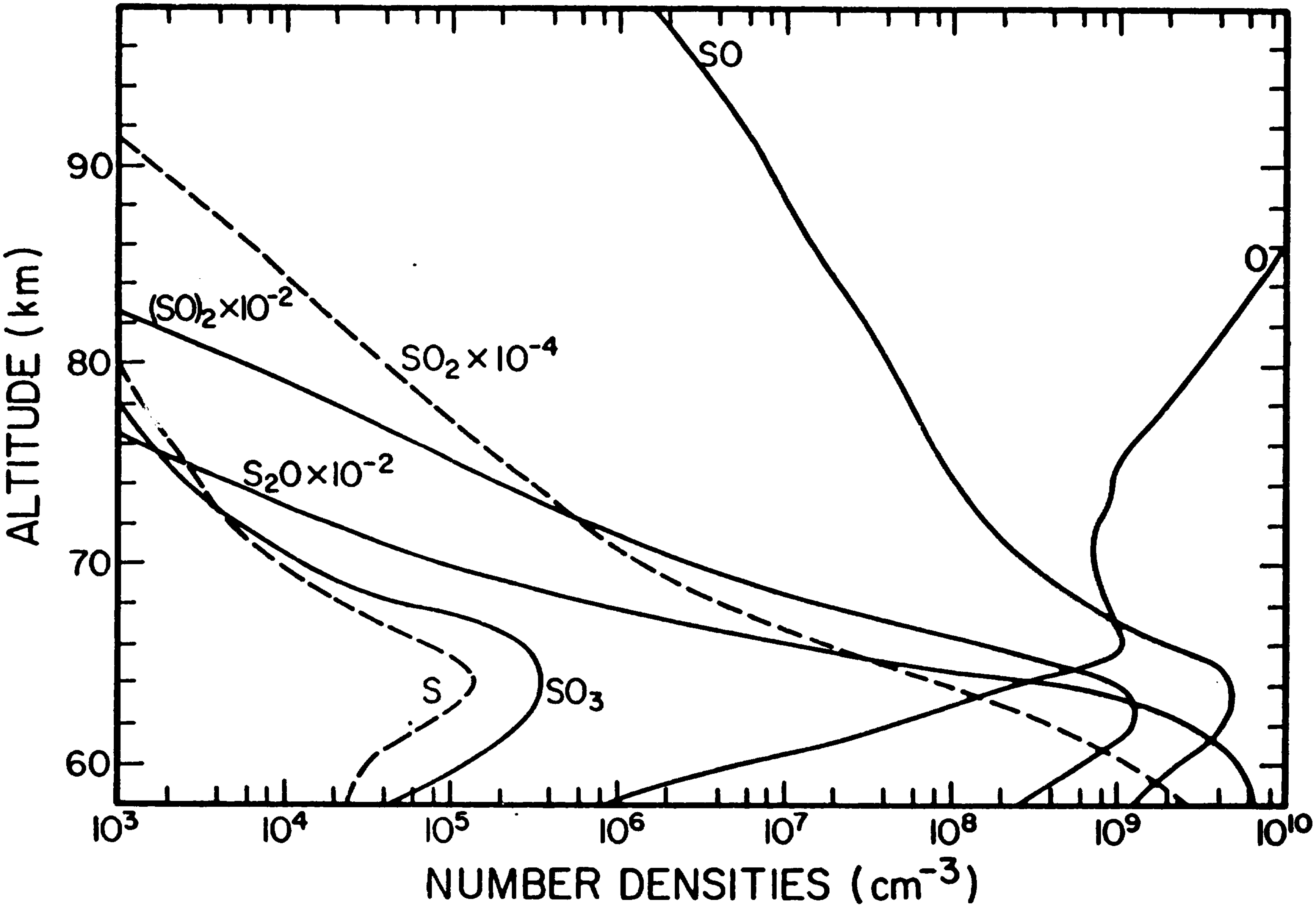

ALTITUDE (km)
90
80
70
60
NUMBER DENSITIES (cm^{-3})
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
10^{11}
SO
$SO_2 \times 10^{-4}$
SO_3
S

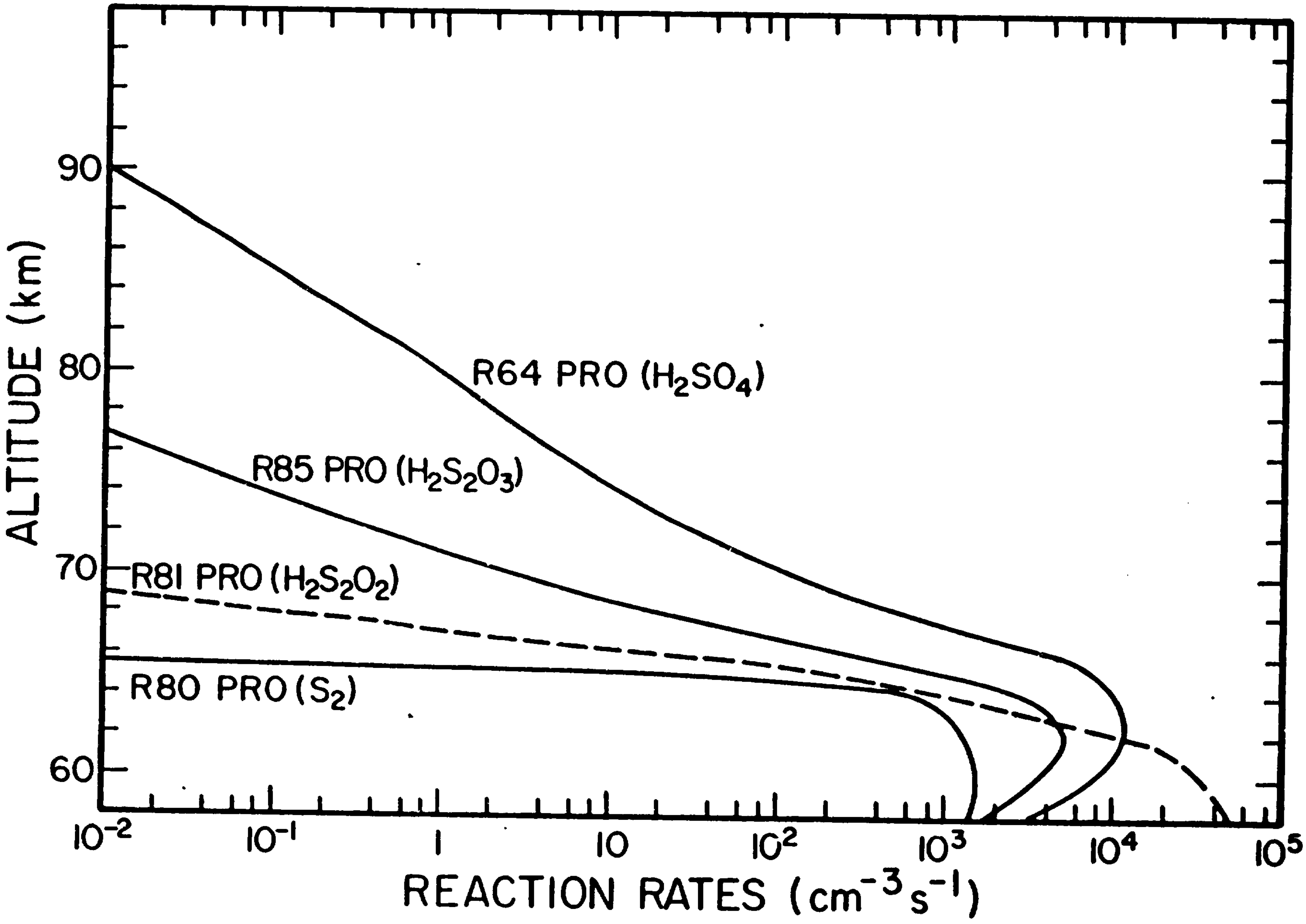

R54 SO + HO2
R9 SO2 + hν
R55 SO + ClO
R56 SO + SO
R50 SO + O + M
ALTITUDE (km)
100
90
80
70
60
REACTION RATES (cm-3 s-1)
10^3
10^4
10^5
10^6
10^7
10^8


ALTITUDE (km)
100
90
80
70
60
R56 SO+ SO
R46 S + O_2
R8 SO + hν
10^2
10^3
10^4
10^5
10^6
10^7
REACTION RATES ($cm^{-3} s^{-1}$)

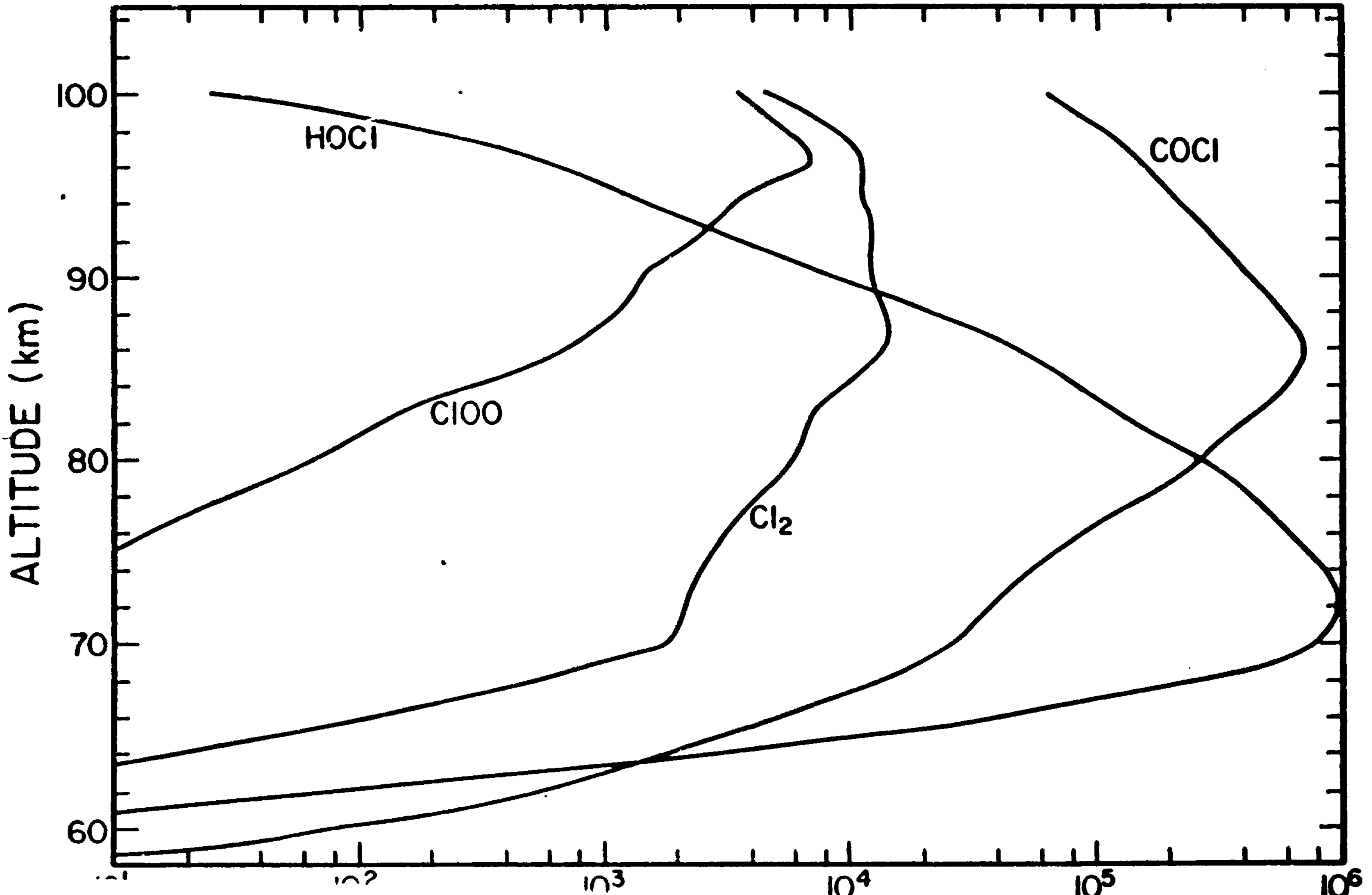

ALTITUDE (km)
100
90
80
70
60
HSO$_3$ • H$_2$O
HSO$_3$
10^4
10^5
10^6
10^7
10^8
10^9
NUMBER DENSITIES (cm^{-3})


R72 $HSO_3 \cdot H_2O + O$
R74 $HSO_3 \cdot H_2O + OH$
R58 $SO_2 + OH + M$
R66 $HSO_3 + O$
R68 $HSO_3 + OH$
R76 $HSO_3 + HSO_3 \cdot H_2O$
ALTITUDE (km)
90
80
70
60
1
10
10^2
10^3
10^4
10^5
10^6
10^7
REACTION RATES ($cm^{-3} s^{-1}$)

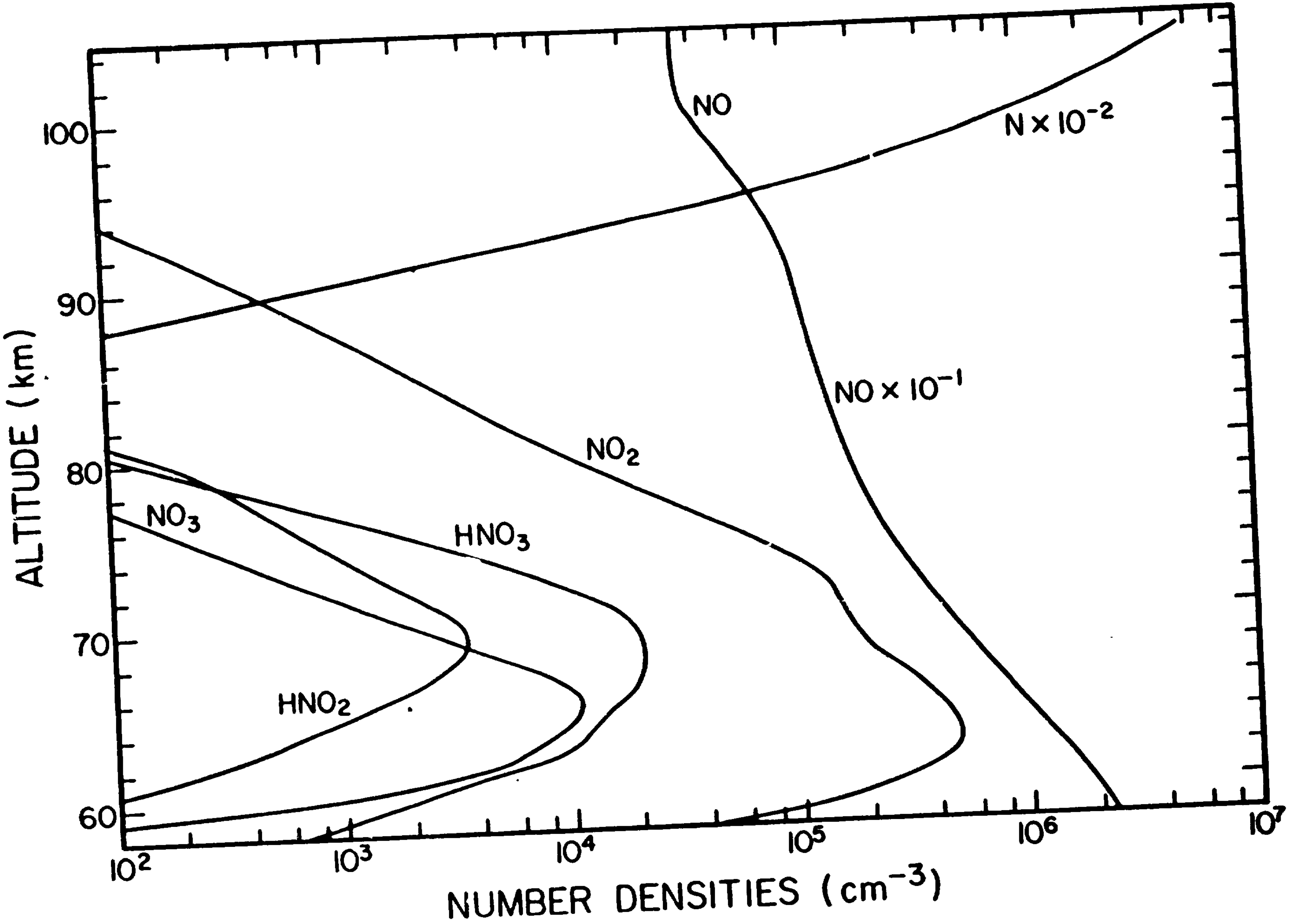

SO
O
$(SO)_2 \times 10^{-2}$
$SO_2 \times 10^{-4}$
$S_2O \times 10^{-2}$
S
SO_3
ALTITUDE (km)
90
80
70
60
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
NUMBER DENSITIES (cm^{-3})



R64 PRO (H_2SO_4)
R85 PRO ($H_2S_2O_3$)
R81 PRO ($H_2S_2O_2$)
R80 PRO (S_2)
ALTITUDE (km)
90
80
70
60
REACTION RATES ($cm^{-3}s^{-1}$)
10^{-2}
10^{-1}
1
10
10^2
10^3
10^4
10^5



HOCl
COCl
ClOO
Cl_2
ALTITUDE (km)
100
90
80
70
60
10^2
10^3
10^4
10^5
10^6


NO
N × 10^{-2}
NO × 10^{-1}
NO$_2$
HNO$_3$
NO$_3$
HNO$_2$
ALTITUDE (km)
100
90
80
70
60
10^2
10^3
10^4
10^5
10^6
10^7
NUMBER DENSITIES (cm^{-3})