NASA CR- 159951

(NASA-CR-159951) THE CHEMISTRY OF VENUS'
ATMOSPHERE Annual Project, Jul. 1977 - Jul.
1978 (Atmospheric and Environmental
Research) 63 p HC A04/MF A01 CSCL 03B
N80-16011
Unclas
G3/91 45809

THE CHEMISTRY OF VENUS' ATMOSPHERE

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July 1978
Annual Project Report for Period
July 1977 to July 1978

Prepared for
GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland 20771

PREFACE

A photochemical model for the Venus atmosphere including oxygen, hydrogen, chlorine and sulfur chemistry is presented. Primary emphasis is placed on the formulation of the sulfur chemistry and its role in the formation of H_2SO_4 molecules for the hydrated sulfuric acid droplet cloud deck of Venus.

The present study both complements and extends the earlier sulfur chemistry of Prinn (1973, 1975) and the hydrogen, chlorine and oxygen chemistry of Sze and McElroy (1975). Sulfur is released by photolysis of COS and oxygen is supplied by photolysis of CO_2. Subsequent reactions oxidize sulfur and lead to formation of H_2SO_4.

The dominant sulfur oxidation process for H_2SO_4 production involves reactions of S with O_2 followed by reactions of SO and SO_2 with atomic oxygen. The odd hydrogen production scheme proposed by Prinn (1973) plays a relatively minor role. The abundance of O_2 controls the rate limiting step in the H_2SO_4 formation sequence. The concentration of SO_2 and COS calculated from the model are comparable above 65 km. The upward flux of COS is balanced by the downward fluxes of SO_2 and H_2SO_4 in approximately equal proportions. The supply of H_2SO_4 may be sufficient to maintain a 10 km thick cloud deck if the sulfuric acid cloud droplets have a residence time of about a few years. Shorter residence time requires either a thinner cloud or additional chemical reactions to increase the efficiency of converting SO_2 into SO_3.

Further studies of the chemical model are warranted to explore the sulfur chemistry. Future measurements on SO_2 abundance would be extremely useful in refining the model results.

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CHAPTER I

INTRODUCTION

Understanding of the composition and structure of the atmosphere of Venus has progressed significantly in recent years. Both earth based astronomy and spacecraft measurements have made important contributions. These measurements have provided observational constraints for development of atmospheric models. Photochemical reaction schemes used in these models have to date placed primary emphasis upon the stability of the CO_2 atmosphere. Several mechanisms, involving catalytic chemistry of odd hydrogen (H, OH, HO_2, H_2O_2) and odd chlorine (Cl, Cl_2, HCl, ClO, ClOO), were successfully employed by McElroy, Sze and Yung (1973) and Sze and McElroy (1975), for recombination of CO_2 in the Venus atmosphere above the visible H_2SO_4 cloud layer. Alternative mechanisms have been proposed by Prinn (1973, 1975), who stressed sulfur photochemistry for production of H_2SO_4 molecules above the cloud, and recombination of CO_2 below the cloud. A more complete photochemical model for the Venus atmosphere would combine the merits of the oxygen, hydrogen and chlorine chemistry of Sze and McElroy with the sulfur chemistry of Prinn. Development of such a numerical model and initial evaluation of it are the subjects of this report.

Interest in exploring this more complete photochemistry for Venus has increased with the realization that updates chemical reaction rates have lowered the efficiency of the catalytic recombination schemes presented by Sze and McElroy (1975). Without other oxygen sinks such as that provided by sulfur, the excess O_2 produced would violate the observed mixing ratio, unless it could be transported downward more rapidly and converted to CO_2 below the cloud layer. Efforts to specify the fraction of the excess O_2 that can be transported below the clouds and the fraction that can be converted into H_2SO_4 above the clouds, are reported.

CHAPTER II

PHOTOCHEMISTRY FOR VENUS

2.1 Structure and Composition of the Atmosphere

The vertical structure and composition of the Venus atmosphere determined by earth-based and spacecraft measurements is rather poorly defined. The major constituent of the atmosphere is CO_2 with a column abundance equal to or in excess of 93% (Vinogradov et al., 1971). Nitrogen and argon are likely candidates for the other major gases that make up most of the remaining 7%. The surface pressure and temperature of Venus are approximately 93 bars and 750° respectively (Marov et al., 1973). The surface is however completely obscured from view by a cloud layer composed of partially hydrated sulfuric acid droplets which is located approximately in the 45-62 altitude range. Vertical profiles for the number density of CO_2 and temperature from the cloud tops to a 100 km altitude are given in Table 1.

The mixing ratios of trace gases which have been detected in the Venus atmosphere or which have measured upper limits, are listed in Table 2. The small concentration of O_2 (<1ppm) and CO (~50ppm) were initially most surprising results, given the ease of producing large amounts of CO and O_2 from photolysis of CO_2. This sparked interest in understanding the stability of the CO_2 atmosphere. The trace species H_2O is much more concentrated below the Venus cloud layer, suggesting that much of the upward flow of water is both photochemically converted into H_2SO_4 and absorbed

Table 1

Number Density and Temperature of the Venus Atmosphere*

Height (km)	N(z) (cm^{-3})	T(z) (^{o}K)
62	6.80(18)	255
64	4.24(18)	246
66	3.17(18)	239
68	2.10(18)	232
70	1.55(18)	225
72	9.99(17)	217
74	7.26(17)	209
76	4.53(17)	200
78	3.22(17)	194
80	1.90(17)	188
82	1.30(17)	184
84	8.17(16)	180
86	4.50(16)	177
88	2.90(16)	175
90	1.73(16)	173
92	9.91(15)	171
94	6.30(15)	170
96	3.67(15)	168
98	2.00(15)	167
100	1.27(15)	166

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* NASA SP-8011 Models of Venus Atmosphere (1972)

Table 2

Abundance of Trace Gases in the Venus Atmosphere

Trace Gas (above clouds)	Mixing Ratio (ppm)	Reference
CO	50	Young (1972)
O_2	<1	Traub & Carleton (1974)
H_2O (above cloud)	0.5-40	Barker (1975)
(below cloud)	10^3-10^4	Rossow & Sagan (1975), Vinogrador et al. (1971)
HCl	0.6	Young (1972)
COS	<1	Cruikshank (1967)
SO_2	<0.035	Cruikshank & Kuiper (1967)
H_2SO_4 (in clouds)	~ 10	Rossow & Sagan (1975)
H_2S	<0.3	Anderson et al. (1969)
HF	<0.01	Young (1972)
He	10	Kumar & Broadfoot (1975)

by the cloud droplets. HCl through photolysis, provides a major source of hydrogen and chlorine to the Venus atmosphere. This large concentration of HCl, together with the small concentration of O_2, is responsible for the lack of an ozone layer in the Venus atmosphere. The abundance of H_2SO_4 molecules above the cloud layer is not known but the approximate amount present below the cloud tops is given. Upper limits are given for other sulfur species that are likely to be present in the atmosphere. Measured values are also given for HF and He, although neither is included in chemical modeling.

The vertical structure and composition of trace gases in the atmosphere reflects an interplay between diffusion, chemical production and chemical loss processes of the various species. Turbulent mixing, which is modeled by eddy diffusion, dominates the vertical transport from the surface of Venus to the homopause (turbopause), located at an altitude of about 130 km. The individual gas species in this region are driven to a constant mixing ratio in the absence of chemical production and loss. The role of global circulation in vertical transport is not clear but it may also be important below the homopause. Molecular diffusion dominates vertical transport from the homopause to the exosphere (at about 200 km), with ballistic transport operating above this altitude level. The lighter gas species therefore have greater relative abundances as the altitude increases, with chemical processes altering this behavior locally.

Chemical modeling to be considered will focus attention upon the altitude range from the cloud tops to 100 km. This is the region where sulfur is actively converted into H_2SO_4 molecules and transported downward to supply the cloud. Reaction schemes for oxygen, hydrogen, chlorine and sulfur chemistry to be used in the Venus atmosphere model are presented below.

2.2 Pre-Sulfur Chemistry

The hydrogen and chlorine chemistry for the Venus atmosphere was developed out of the need to understand the stability of the CO_2 atmosphere. Figure 1 shows the photodissociation rate for CO_2, HCl and H_2O in the Venus atmosphere as calculated by McElroy, Sze and Yung (1973). The column dissociation rate for CO_2 is about 1×10^{13} molecules cm^{-2} sec^{-1}, a value capable of depleting Venus of its entire CO_2 atmosphere in a few million years.

Photochemical models using simple oxygen chemistry given by the reaction scheme (2.2.1) were unsuccessful in recombining CO_2.

$$CO_2 + h\nu \rightarrow CO + O \qquad (2.2.\ 1a)$$

$$O + O + CO_2 \rightarrow O_2 + CO_2\ . \qquad (2.2.\ 1b)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (2.2.\ 1c)$$

$$CO + O + M \rightarrow CO_2 + M \qquad (2.2.\ 1d)$$

Reaction (2.2. 1c) is endothermic at Venus temperatures, while reaction (2.2. 1d) is operative, but has an extremely small rate

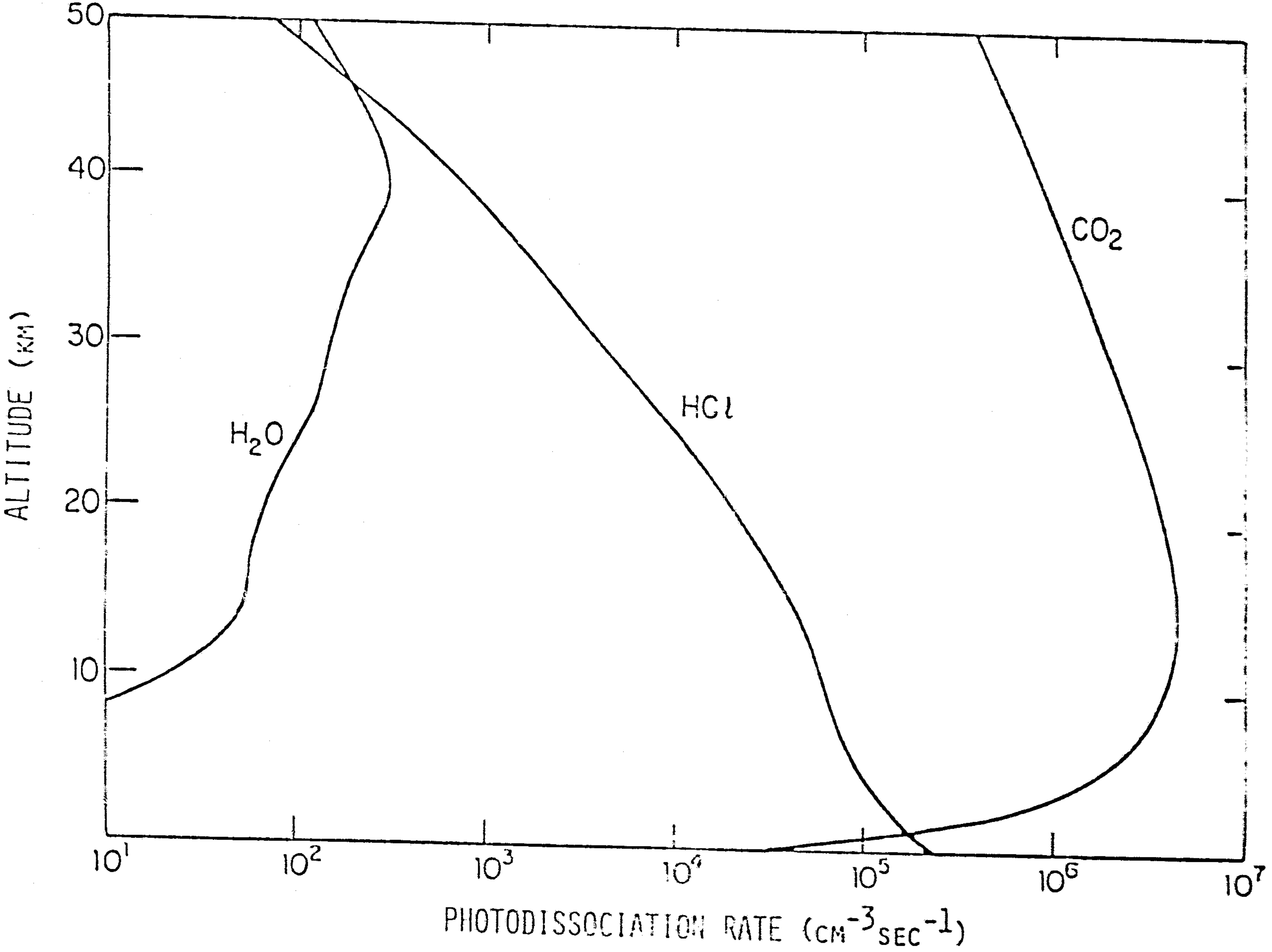

Figure 1.

Photodissociation Rates for CO_2, HCl and H_2O. The altitude is measured from the cloud tops, assumed to be 62 km above the Venus surface.

constant because it is spin forbidden.

A more complex chemistry involving other atoms was therefore considered to explain the stability of CO_2. Successful catalytic recombination schemes for this purpose using hydrogen and chlorine chemistry were given by Sze and McElroy (1975). In their model, removal of CO proceeded by two main paths:

$$\begin{aligned} H + O_2 + CO_2 &\rightarrow HO_2 + CO_2 \\ O + HO_2 &\rightarrow OH + O_2 \\ CO + OH &\rightarrow CO_2 + H \end{aligned} \tag{2.2.2}$$

and

$$\begin{aligned} 2\ \{ H + O_2 + CO_2 &\rightarrow HO_2 + CO_2 \} \\ HO_2 + HO_2 &\rightarrow H_2O_2 + O_2 \\ h\nu + H_2O_2 &\rightarrow 2OH \\ 2\ \{ CO + OH &\rightarrow CO_2 + H \} \end{aligned} \tag{2.2.3}$$

The first corresponds to the net reaction

$$H + CO + O \rightarrow H + CO_2 \tag{2.2.4}$$

while the second is equivalent to

$$2H + 2CO + O_2 \rightarrow 2H + 2CO_2 \tag{2.2.5}$$

The necessary source of hydrogen is provided by photolysis of HCl

$$h\nu + HCl \rightarrow H + Cl \tag{2.2.6}$$

followed by

$$Cl + H_2 \rightarrow HCl + H \tag{2.2.7}$$

were molecular hydrogen consumed in (2.2.7) is produced above the cloud by

$$H + HO_2 \rightarrow H_2 + O_2 \tag{2.2.8}$$

and supplied from below by an upward flux. Both recombination schemes (2.2.2) and (2.2.3) depend upon the odd hydrogen species HO_2. Similiar reaction schemes exist for chlorine using the radical ClO, but they are of lesser importance. A list of relevant reactions for oxygen, hydrogen and chlorine chemistry is given in Table 3.

New kinetic data on chemical reactions available since 1975 have shown that the rate of the reaction

$$HO_2 + Cl \rightarrow HCl + O_2 \tag{2.2.9}$$

is about 100 times larger than the value adopted in the work of Sze and McElroy (1975). The increase in this reaction rate reduces the efficiency of the catalytic recombination scheme in two ways. First it reduces the concentrations of HO_2 and Cl. Second it removes two chemically active species and replaces them with the more stable molecules HCl and O_2. The concentrations of O, O_2 and CO must then increase. To avoid violating observational constraints, the excess CO and O_2 must be transported downward and converted below the cloud deck by unspecified thermochemical processes into CO_2. The CO_2 below the clouds is then recycled by upward transport. If however sulfur chemistry is added to the model, the excess O_2 may alternatively be able to locally supply oxygen for formation of H_2SO_4 molecules.

Table 3

Reaction	Rate	Reference
$CO_2 + h\nu \rightarrow CO + O$	$J_1 = 1\ (-6)$	(calculated)
$H_2O_2 + h\nu \rightarrow 2OH$	$J_2 = 1.1\ (-4)$	(calculated)
$HCl + h\nu \rightarrow H + Cl$	$J_3 = 3.9\ (-6)$	(calculated)
$Cl_2 + h\nu \rightarrow 2Cl$	$J_4 = 2.7\ (-3)$	(calculated)
$O_2 + h\nu \rightarrow O + O$	$J_5 = 5\ (-6)$	(calculated)
$O_3 + h\nu \rightarrow O_2 + O$	$J_6 = 8.8\ (-3)$	(calculated)
$O + O + CO_2 \rightarrow O_2 + CO_2$	$k_1 = 3 \times 10^{-33} (T/300)^{-2.9}$	Reeves et al. (1960)
$O + OH \rightarrow H + O_2$	$k_2 = 5\ (-11)$	Kaufman (1964)
$H + O_2 + CO_2 \rightarrow HO_2 + CO_2$	$k_3 = 2 \times 10^{-31} (T/273)^{-1.3}$	Baulch et al. (1969)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_4 = 3.5\ (-12)$	Hudson (1977)
$OH + CO \rightarrow H + CO_2$	$k_5 = 2 \times 10^{-13} \exp(-500/T)$	Hudson (1977)
$OH + HO_2 \rightarrow H_2O + O_2$	$k_6 = 4\ (-11)$	Burrows et al. (1977)
$OH + HCl \rightarrow H_2O + Cl$	$k_7 = 2 \times 10^{-13} \exp(-310/T)$	Zahniser et al. (1974)
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$k_8 = 1 \times 10^{-11} \exp(-750/T)$	Hack et al. (1975)
$O + HO_2 \rightarrow OH + O_2$	$k_9 = 4.0\ (-11)$	Burrows et al. (1977)
$O + O_2 + CO_2 \rightarrow O_3 + CO_2$	$k_{10} = 1.4 \times 10^{-33} (T/300)^{-2.5}$	Kaufman (1969)
$H + HO_2 \rightarrow H_2 + O_2$	$k_{11} = 1.4 (-11)$	McElroy & Donahue (1972)
$OH + OH \rightarrow H_2O + O$	$k_{12} = 1.4 (12)$	Clyne and Down (1974)
$Cl + H_2 \rightarrow HCl + H$	$k_{13} = 8 \times 10^{-11} \exp(-2480/T)$	McCrumb & Kaufman (1972)

Table 3
(continued)

Reaction	Rate	Reference
$Cl + Cl + CO_2 \rightarrow Cl_2 + CO_2$	$k_{14} = 2.7 \times 10^{-32}$	Bader & Ogryzlo (1964)
$Cl + O_3 \rightarrow ClO + O_2$	$k_{15} =$ 1.[illegible] (-11)	Clyne & Watson (1974)
$ClO + O \rightarrow Cl + O_2$	$k_{16} =$ 4.[illegible] (-11)	Zahniser & Kaufman (1977)
$ClO + CO \rightarrow CO_2 + Cl$	$k_{17} = 1.7\ (-15)$	Walker (1972), Harber (1972)
$ClO + ClO + CO_2 \rightarrow Cl_2 + O_2 + CO_2$	$k_{18} =$ 1.[illegible] (-31)	Johnston et al. (1969)
$Cl + HO_2 \rightarrow HCl + O_2$	$k_{19} =$ 3.[illegible] (-11)	DeMore (1976)
$H + O_3 \rightarrow OH + O_2$	$k_{20} = 2.6\ (-11)$	Kaufman (1964)
$O + O_3 \rightarrow 2O_2$	$k_{21} = 1.3 \times 10^{-11} \exp(-2140/T)$	McCrumb & Kaufman (1972)

2.3 Sulfur Chemistry

Formation of H_2SO_4 molecules in the Venus atmosphere may be limited by the supply of hydrogen, oxygen and sulfur atoms. In the sulfur chemistry to be considered, hydrogen is supplied above the clouds by photolysis of HCl and from below the clouds by an upward flux of H_2 and H_2O. Oxygen is supplied by photolysis of CO_2 so that the downward flux of H_2SO_4 must be less than the column dissociation rate of CO_2

$$\int_{Z_B}^{\infty} J_{CO_2} N_{CO_2}\, dZ \approx 1.5\text{x}10^{13}\ \text{cm}^{-2}\ \text{sec}^{-1} \tag{2.3.1}$$

Sulfur is supplied above the clouds by photolysis of COS, a postulated but undetected molecule in the Venus atmosphere. COS is postulated to be reformed by thermochemical processes below the cloud deck and returned by an upward flux. The upper limit on the mixing ratio of COS above the cloud layer is about 10^{-6}.

Sulfur Reaction Scheme

An explicit photochemical reaction scheme for production of H_2SO_4 based on these ideas was first introduced by Prinn (1973). The Prinn scheme consists of six reactions:

$$\left.\begin{array}{ll}
COS + h\nu \rightarrow CO + S('D) & \text{(a)} \\
S('D) + CO_2 \rightarrow S + CO_2 & \text{(b)} \\
S + O_2 \rightarrow SO + O & \text{(c)} \\
SO + OH \rightarrow SO_2 + H & \text{(d)} \\
SO_2 + HO_2 \rightarrow SO_3 + H & \text{(e)} \\
SO_3 + H_2O + CO_2 \rightarrow H_2SO_4 + CO_2 & \text{(f)}
\end{array}\right\} \tag{2.3.2}$$

The rate limiting step in scheme (2.3.2) is the reaction (2.3.2e). The number density of HO_2 is about 10^9 cm^{-3} at cloud tops, dropping rapidly with increasing altitudes according to Sze and McElroy (1975). The rate constant for this reaction is very slow, with a value 9×10^{-16} cm^3 s^{-1}. The conversion of SO_2 to H_2SO_4 is therefore rather inefficient. A modest production rate for H_2SO_4 is insured only by requiring an appreciable concentration of SO_2 which might however violate the observed upper limits of SO_2 column abundance.

An alternate sulfur reaction scheme may be summarized as follows.

$$\begin{array}{llr} COS + h\nu \rightarrow CO + S('D) & (a) & \\ S('D) + CO_2 \rightarrow S + CO_2 & (b) & \\ S + O_2 \rightarrow SO + O & (c) & \\ SO + O + M \rightarrow SO_2 + M & (d) & (2.3.3) \\ SO_2 + O + M \rightarrow SO_3 + M & (e) & \\ SO_3 + H_2O + M \rightarrow H_2SO_4 + M & (f) & \end{array}$$

The above scheme involves only sulfur and oxygen species, in contrast to reaction scheme (2.3.2) which involves odd hydrogen, in addition to oxygen and sulfur chemistry. The rate limiting step in scheme (2.3.3) is the reaction (2.3.3e). The rate constant for this reaction is about 7×10^{-33} cm^6 sec^{-1}, which is equivalent to a two body rate of about 5×10^{-14} cm^3 sec^{-1}, a moderately fast rate.

The concentration of atomic oxygen is significantly enhanced because of the major revisions in rate constants as discussed in Section 2.2. Moreover, the concentration of O would be further enhanced by including the reaction

$$S + O_2 \rightarrow SO + O \qquad (2.3.4)$$

which represents an additional source of oxygen below 70 km. Figure 2 shows the importance of atomic oxygen production due to reaction (2.3.4) relative to CO_2 photolysis. It appears that scheme (2.3.3) might provide an interesting alternative to scheme (2.3.2), as proposed by Prinn (1973, 1975).

The complete chemical model to be explored in this study is given in Table 4 and incorporates all reactions from both of these schemes. Additional sulfur reactions are also included. Rate constant subscripts are numbered consecutively with those in Table 3. The rate k_{28} is unmeasured and an estimated value is given. Reaction k_{31} is an effective reaction, a composite of the reaction

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad (2.3.5)$$

followed by photolysis of HSO_3. The reaction J_8 is not effective in the lower portion of the atmosphere where sulfur has its impact because CO_2 provides an optically thick path for photons below wavelengths of about 2100 Å. Rate constants k_{32} and k_{33} are treated as parameters and simulate postulated heterogeneous production processes for H_2SO_4.

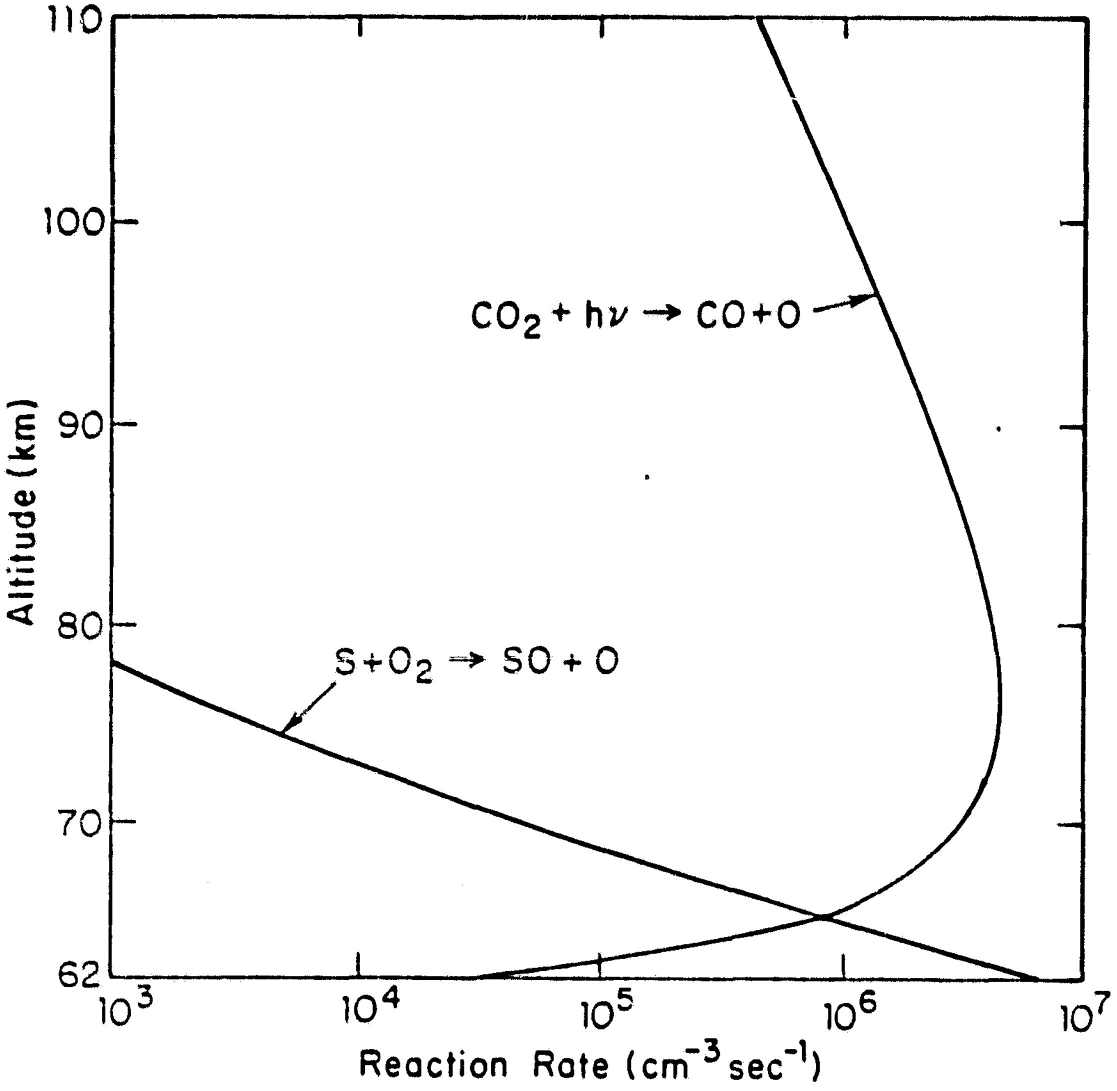

Figure 2.

Production Rate for Atomic Oxygen. The rate of creation of oxygen atoms by photolysis of CO_2 and the reaction of S and O_2 are indicated as a function of altitude.

Table 4

Reaction	Rate	Reference
$COS + h\nu \rightarrow CO + S$	$J_7 = 1.2(-5)$	Prinn (1973)
$S + O_2 \rightarrow SO + O$	$k_{22} = 2.2(-12)$	Davis et al. (1972)
$SO + OH \rightarrow SO_2 + H$	$k_{23} = 1.2(-10)$	Fair & Thrush (1969)
$SO + O + M \rightarrow SO_2 + M$	$k_{24} = 8.5\ (-31)$	Schofield (1973)
$SO + O_2 \rightarrow SO_2 + O$	$k_{25} = 3 \times 10^{-13} \exp(-2800/T)$	Schofield (1973)
$SO + O_3 \rightarrow SO_2 + O_2$	$k_{26} = 2.5 \times 10^{-12} \exp(-1050/T)$	Schofield (1973)
$SO + SO \rightarrow SO_2 + S$	$k_{27} = 8.3\ (-14)$	Chung, Calvert, Bottenheim (1974)
$SO + HO_2 \rightarrow SO_2 + OH$	$k_{28} = 1.0\ (-14)$	(estimated)
$SO_2 + HO_2 \rightarrow SO_3 + OH$	$k_{29} = 9.0\ (-16)$	Payne et al. (1973)
$SO_2 + O + M \rightarrow SO_3 + M$	$k_{30} = 1 \times 10^{-33} \exp(500/T)$	Schofield (1973)
$SO_2 + OH + M \rightarrow SO_3 + H + M$	$k_{31} = 3.0\ (-32)$	(see text)
$SO_2 + h\nu \rightarrow SO + O$	$J_8 < 10^{-8}$	(see text)
$SO_2 + H_2O_2 + M \rightarrow H_2SO_4 + M$	$k_{32} = 1.5\ (-34)$	(see text)
$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$	$k_{33} = 1.5\ (-33)$	(see text)

CHAPTER III

MODEL DEVELOPMENT

3.1 Atmospheric Model

A one dimensional photochemical model similiar to the one used by Sze and McElroy (1975), has been developed for the Venus' atmosphere. The number density for the ith species, n_i, is governed by the steady state continuity and diffusion equations:

$$\frac{d\phi_i}{dZ} = P_i - L_i n_i \quad , \qquad (3.1.1.a)$$

and

$$\phi_i = -K \left(\frac{dn_i}{dZ} + \frac{n_i}{H_{av}} + \frac{n_i}{T}\frac{dT}{dZ}\right)$$

$$-D_i \left(\frac{dn_i}{dZ} + \frac{n_i}{H_i} + (1 + \alpha_i)\frac{n_i}{T}\frac{dT}{dZ}\right) \quad , \qquad (3.1.1.b)$$

where P_i and $L_i\ n_i$ represent the production and loss rate (molecule $cm^{-3}\ s^{-1}$); K and D_i represent the eddy and molecular diffusion coefficients, H_{av} and H_i represent the average scale height and species scale height and α_i is the effective thermal diffusion coefficient.

The eddy diffusion coefficient was assumed to have the form

$$\begin{aligned} K(Z) &= K_o\left(\frac{n(Z)}{n(Z_B)}\right)^{-\frac{1}{2}} & Z_B \le Z \le Z^* \\ &= K^* & Z^* \le Z \le Z_T \end{aligned} \qquad (3.1.2)$$

where $n(Z)$ is the number density of the CO_2 background gas and $K^* = K(Z^*)$. The molecular diffusion coefficient D_i has the form

$$D_i(Z) = \frac{3}{16Q_i}\,\frac{1}{n(Z)}\left(\frac{2kT(Z)}{\mu_i}\right)^{\frac{1}{2}} \tag{3.1.3}$$

where Q_i is the rigid sphere cross section for collision of the i^{th} species with the background gas, and μ_i is the reduced mass for the i^{th} species mass m_i and the background gas mass m. Vertical profiles for the number density $n(Z)$ and temperature $T(Z)$ of CO_2 are given in Table 1 for altitudes from the cloud tops (62 km) to 100 km.

The altitude dependence for the scale heights are given by

$$H_{av} = \frac{kT(Z)}{mg} \tag{3.1.4}$$

$$H_i = \frac{kT(Z)}{m_i g} \tag{3.1.5}$$

where g is the acceleration of gravity at the Venus surface. The coefficient α_i is effectively zero except for hydorgen.

Eddy diffusion dominates molecular diffusion below the homopause (∿ 130 km), while molecular diffusion is dominant above this level to the exosphere. The lower boundary, Z_B, is chosen to be at 62 km and the upper boundary Z_T at 100 km, below which sulfur chemistry is incorporated in the model.

3.2 Numerical Procedure

Solutions for the diffusion equation can be divided into two categories.

(1) those for species involved in chemical reactions that are fast compared to diffusion processes and

(2) those for species involved in chemical loss times which are only comparable or slower than the characteristic diffusion times.

For the first category, the number densities n_i may be obtained by solving a set of non-linear coupled algebraic equations.

$$P_i = L_i n_i$$

A generalized Newton's method was employed to slove these equations.

In the later category the second order differential equation (3.1.1) for n_i must be solved. A finite difference method is applied and an iterative procedure adopted to obtain a solution for these species. Two boundary conditions are required for each equation and must be chosen in a consistent way so as not to overspecify or underspecify the solution for the set of equations.

For the photochemical reaction schemes adopted for oxygen, hydrogen, chlorine (see Table 3) and sulfur (see Table 4), there are 11 species in the first category and 7 species in the second category. The fast species are O, O_3, S, SO, SO_3, OH, H, H_2O_2, HO_2, ClO and Cl_2. The slow species are O_2, CO, HCl, Cl, COS, SO_2, and H_2SO_4. The two remaining trace species H_2 and H_2O are assumed to have constant mixing ratios of 2×10^{-7} and 10^{-6} respectively. The chemical loss terms are given in Table 5 for the photochemical reaction scheme of Table 3 and Table 4.

3.3 Boundary Conditions

The number density of each slow trace gas species (see section 3.2) is governed by the diffusion equation (3.1.1). For each species, two boundary conditions are required for a unique solution. Either the flux or mixing ratio of each species may be specified at the lower boundary ($Z = Z_B$). The flux is usually specified at the top boundary ($Z = Z_T$).

Boundary conditions must be chosen so as to provide number density profiles consistent with observations. For Venus (see Table 2) average column mixing ratios are known for CO and HCl. Only upper limit values have been measured for O_2, COS and SO_2. Boundary conditions are therefore not well defined for most of the slow species. More measurements are clearly needed to eliminate this difficulty.

Solutions to be explored here are based upon the assumption that photolysis of CO_2 and COS above the cloud layer provide the major sources of oxygen and sulfur for H_2SO_4 formation, excluding an upward flux of H_2O. It then follows that fluxes of CO, SO_2,O_2 and H_2SO_4 must be downward. Conservation of atoms then requiring an upward flux for COS, CO_2 and H_2O. The fluxes of O_2, CO, HCl, Cl, COS and SO_2 are taken to be zero at the top boundary ($Z = Z_T$).

Table 5

Production and Loss Terms for Trace Species

Species	Production Pi	Loss Li
O	$J_1(CO_2)+k_{12}(OH)^2+2J_5(O_2)$ $+J_6(O_3)+k_{22}(S)(O_2)$ $+k_{25}(SO)(O_2)+J_8(SO_2)$	$2k_1(CO_2)(O)+k_2(OH)$ $+k_9(HO_2)+k_{10}(CO_2)(O_2)$ $+k_{16}(ClO)+k_{21}(O_3)$ $+k_{24}(CO_2)(SO)+k_{30}(CO_2)(SO_2)$
O_2	$k_1(CO_2)(O)^2+k_2(O)(OH)$ $+k_4(HO_2)^2+k_6(OH)(HO_2)$ $+k_9(O)(HO_2)+k_{11}(H)(HO_2)$ $+k_{16}(ClO)(O)+k_{18}(CO_2)(ClO)^2$ $+k_{19}(Cl)(HO_2)+k_{21}(O)(O_3)$	$J_5+k_3(CO_2)(H)$ $+k_{22}(S)+k_{25}(SO)$
O_3	$k_{10}(CO_2)(O_2)(O)$	$k_{15}(Cl)+J_6+k_{20}(H)$ $+k_{21}(O)+k_{26}(SO)$
OH	$2J_2(H_2O_2)+k_9(O)(HO_2)$ $+k_{20}(H)(O_3)+k_{28}(SO)(HO_2)$ $+k_{29}(SO_2)(HO_2)$	$k_2(O)+k_5(CO)+k_6(HO_2)$ $+k_7(HCl)+k_8(H_2O_2)$ $+2k_{12}(OH)+k_{23}(SO)$ $+k_{31}(CO_2)(SO_2)$
H	$k_2(O)(OH)+k_5(OH)(CO)$ $+J_3(HCl)+k_{13}(Cl)(H_2)$ $+k_{23}(SO)(OH)+k_{31}(CO_2)(SO_2)(OH)$	$k_3(CO_2)(O_2)+k_{11}(HO_2)$ $+k_{20}(O_3)$

Table 5 (cont.)

Species	Production Pi	Loss Li
H_2O_2	$k_4(HO_2)^2$	$J_2+k_8(OH)$ $+k_{32}(CO_2)(SO_2)$
HO_2	$k_3(CO_2)(H)(O_2)+k_8(OH)(H_2O_2)$	$2k_4(HO_2)+k_6(OH)+k_9(O)$ $+k_{11}(H)+k_{19}(Cl)+k_{28}(SO)$ $+k_{29}(SO_2)$
Cl	$J_3(HCl)+k_7(OH)(HCl)$	$k_{13}(H_2)+k_{19}(HO_2)$
ClO	$k_{15}(Cl)(O_3)$	$k_{16}(O)+k_{17}(CO)$ $+2k_{18}(CO_2)(ClO)$
Cl_2	$k_{14}(CO_2)(Cl)^2+k_{18}(CO_2)(ClO)^2$	J_4
COS	-	J_7
S	$J_7(COS)+k_{27}(SO)^2$	$k_{22}(O_2)$
SO	$k_{22}(S)(O_2)+J_8(SO_2)$	$k_{23}(OH)+k_{24}(CO_2)(O)$ $+k_{25}(O_2)+k_{26}(O_3)$ $+2k_{27}(SO)+k_{28}(HO_2)$

Table 5 (cont.)

Species	Production Pi	Loss Li
SO_2	$J_7(COS)$	$k_{29}(HO_2)+k_{30}(CO_2)(O)$ $+k_{31}(CO_2)(OH)+k_{33}(CO_2)(H_2O)$
SO_3	$k_{29}(SO_2)(HO_2)+k_{30}(CO_2)(O)(SO_2)$ $+k_{31}(CO_2)(SO_2)(OH)$	$k_{33}(CO_2)(H_2O)$
H_2SO_4	$k_{32}(CO_2)(H_2O_2)(SO_2)$ $+k_{33}(CO_2)(H_2O)(SO_3)$	-
CO	$J_1(CO_2)+J_7(COS)$	$k_5(OH)+k_{17}(ClO)$
HCl	$k_{13}(Cl)(H_2)+k_{19}(Cl)(HO_2)$	$J_3+k_7(OH)$

Boundary conditions for the lower boundary are summarized in Table 6, where f_i and ϕ_i denote the mixing ratio and flux of the ith species respectively. At this boundary, a range of values will be considered for the O_2 and COS mixing ratios. The mixing ratios of CO and HCl are chosen so as to agree with observations. The chlorine number density n_{Cl}, is assumed to have its chemical equilibrium value. The downward flux of SO_2 is set equal to a fraction α of the upward COS flux, where

$$0 < \alpha < 1$$

The diffusion equation (3.1.1) is not solved for the species H_2SO_4. To determine a number density profile for H_2SO_4 requires either specification of its mixing ratio at boundary (an answer to be hopefully deduced) or specification of a chemical loss process such as would occur by condensation of H_2SO_4 above the cloud tops. The downward flux of H_2SO_4 may be calculated without specification of boundary conditions and is sufficient to evaluate the physical parameters to be defined in section 3.4.

3.4 Discussion of the Physical Processes

The major questions raised by the addition of sulfur chemistry to the oxygen, hydrogen and chlorine chemistry for Venus can be understood by considering the fate of oxygen atoms produced by photolysis of CO_2 above the Venus cloud layer. The column production rate of oxygen (the number of oxygen atoms produced per cm^2 per sec) above the cloud layer is given by

$$P_O = \int_{Z_B}^{\infty} L_{CO_2}\, n_{CO_2}\, dZ \qquad (3.4.1)$$

Table 6

Lower Boundary Conditions for the Slow Trace Species

Species	Boundary Conditions
O_2	$10^{-8} < f_{O_2} < 10^{-7}$
CO	$f_{CO} \approx 5 \times 10^{-5}$
HCl	$f_{HCl} = 6 \times 10^{-7}$
Cl	$n_{Cl} = P_{Cl} / L_{Cl}$
COS	$10^{-10} < f_{COS} < 10^{-6}$
SO_2	$\phi_{SO_2} = - \lambda \phi_{COS}$

Some of these oxygen atoms cycle through the hydrogen and chlorine catalytic recombination schemes and react with CO to reform CO_2. The column loss of O by these processes is given by

$$L_O = \int_{Z_B}^{\infty} P_{CO_2} dZ \quad . \qquad (3.4.2)$$

If the CO_2 recombination schemes is incomplete (i.e. $P_O < L_O$), the excess oxygen must be transported below the cloud tops by downward fluxes of oxygen bearing species, where, through unidentified thermochemical processes, it is converted into CO_2 and COS and recycled upward. In the chemistry under consideration, this excess oxygen may be removed by downward fluxes of O_2, SO_2 and H_2SO_4. In addition to this an upward flux of H_2O at the cloud tops may provide a partial source of oxygen in the production of H_2SO_4 through the reaction

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \qquad (3.4.3)$$

A conservation of oxygen atoms above the cloud tops then requires that

$$P_O - L_O + 2\phi_{O_2} + 2\phi_{SO_2} + 4\phi_{H_2SO_4} + \phi_{H_2O} = 0 \qquad (3.4.4a)$$

where the fluxes ϕ_{O_2}, ϕ_{SO_2} and $\phi_{H_2SO_4}$ are directed downwards and the flux ϕ_{H_2O} directed upwards. Dividing this expression by P_O, we have

$$1 - X_{cat} - X_{O_2} - X_{SO_2} - X_{H_2SO_4} = 0 \qquad (3.4.4b)$$

where

$$X_{cat} = L_O/P_O \tag{3.4.5a}$$

$$X_{O_2} = -(2\phi_{O_2})/P_O \tag{3.4.5b}$$

$$X_{SO_2} = -(2\phi_{SO_2})/P_O \tag{3.4.5c}$$

$$X_{H_2SO_4} = -(4\phi_{H_2SO_4} + \phi_{H_2O})/P_O \tag{3.4.5d}$$

The quantity X_{cat} is the fraction of the oxygen, produced by photolysis of CO_2 above the cloud tops, which is catalytically reconverted to CO_2 above the cloud tops. For 100% conversion $X_{cat}=1$. The quantities X_{O_2}, X_{SO_2} and $X_{H_2SO_4}$ are the fractions of the oxygen produced by photolysis of CO_2 which are transported below the cloud tops by downward fluxes of O_2, SO_2 and H_2SO_4 respectively.

The efforts of Sze and McElroy (1975), which included no sulfur chemistry, emphasized the case where $X_{cat} \to 1$ and $X_{O_2} \to 0$ whereas the efforts of Prinn (1973,1975), with no hydrogen and chlorine chemistry, emphasized the case where $X_{H_2SO_4} \to 1$. Values for the parameters X_{cat}, X_{O_2}, X_{SO_2} and $X_{H_2SO_4}$ which include the coupling between oxygen, hydrogen, chlorine and sulfur photochemistry are sought for the model given in Tabel 3 and Table 4.

The efficiency of the sulfur chemistry in producing H_2SO_4 molecules may be better understood by considering the fate of a sulfur atom produced by photolysis of COS above the Venus cloud layer. This is accomplished by considering the general conservation relations given in Table 7 for the 5 different atoms, O, S, C, Cl and H which make up all the chemical species under consideration. The quantity ϕ_E in Table 7 is the escape flux of H at the Venus exosphere. Notice that the relation (3.4.4) derived earlier is nothing more than the conservation relation for oxygen atoms in Table 7, where ϕ_{CO} and ϕ_{COS} have been eliminated by the carbon conservation relation.

To explore the sulfur budget, we introduce the parameter α (see section 3.3) such that

$$\phi_{SO_2} = -\alpha\phi_{COS} \qquad (3.4.6a)$$

$$\phi_{H_2SO_4} = -(1-\alpha)\phi_{COS} \qquad (3.4,6b)$$

These expressions for the flux of SO_2 and H_2SO_4 automatically satisfies the sulfur atom conservation relation. Eliminating ϕ_{CO_2}, ϕ_{SO_2} and $\phi_{H_2SO_4}$ from the oxygen atom conservation relations, (3.4.6a) and (3.4.6b) we obtain

$$-\frac{\phi_{CO}}{\phi_{COS}} = (5-2\alpha) - 2\frac{\phi_{O2}}{\phi_{COS}} - \frac{\phi_{H2O}}{\phi_{COS}} \qquad (3.4.7)$$

For simplicity, consider that the hydrogen conservation relation is satisfied to first order by an upward flux of H_2O and a downward flux of H_2SO_4. For this situation (3.4.7) becomes

$$\left|\frac{\phi_{CO}}{\phi_{COS}}\right| = (4-\alpha) + 2\left|\frac{\phi_{O_2}}{\phi_{COS}}\right| \qquad (3.4.8)$$

Table 7

Conservation Relations for O, S, C, Cl and H Atoms

O: $2\phi_{O_2} + \phi_{CO} + \phi_{COS} + 2\phi_{SO_2} + 4\phi_{H_2SO_4} + 2\phi_{CO_2} + \phi_{H_2O} = 0$

S: $\phi_{COS} + \phi_{SO_2} + \phi_{H_2SO_4} = 0$

C: $\phi_{CO} + \phi_{COS} + \phi_{CO_2} = 0$

H: $2\phi_{H_2SO_4} + 2\phi_{H_2O} \quad \phi_{HCl} + 2\phi_{H_2} = \phi E$

C: $\phi_{HCl} + \phi_{Cl} = 0$

where ϕ_{CO} and ϕ_{O_2} were assumed to be downward directed fluxes (negative) and ϕ_{COS} an upward flux at the cloud tops. For the extreme case where $X_{H_2SO_2} = 1$ (i.e. $\alpha = 0$, $\phi_{O_2} = 0$) at the cloud tops, $|\phi CO/\phi COS| = 4$, $\phi CO_2 = 0$, $|\phi H_2SO_4/\phi COS| = 1$, $|\phi H_2O/\phi COS| = 1$ and $|\phi CO_2/\phi_{COS}| = 3$ so that the over all chemical reaction below the cloud tops is characterized by

$$4CO + H_2SO_4 \rightarrow 3CO_2 + COS + H_2O \qquad (3.4.9)$$

This chemical reaction was first suggested by Prinn (1973) for thermochemical formation of CO_2, COS and H_2O below the cloud layer. For the other extreme case $X_{O_2} >> X_{SO_2}$ or $X_{H_2SO_4}$ (i.e. $|\phi O_2/\phi_{COS}| \sim 1$, $\phi COS \sim \phi SO_2 \sim \phi H_2SO_4$) at the cloud tops, $|\phi CO/\phi CO_2|$ 1, $|\phi O_2/\phi CO_2| \sim \frac{1}{2}$ so that the overall chemical reaction below the cloud layer is

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (3.4.10)$$

This is the effective reaction consistent with the modeling of Sze and McElroy (1975).

The real Venus photochemical model will produce results immediate to these two extreme cases. H_2O molecules required in the formation of H_2SO_4 by reaction (3.4.3) may be either produced above the clouds or supplied by an upward flux from below the cloud.

CHAPTER IV

RESULTS

4.1 Pre-Sulfur Chemistry

The atmospheric model used in this section is summarized in Table 1. The chemical model is presented in Table 3. This is similar to the model used by Sze and McElroy (1975) with the exception of several updated rate constant values. The eddy diffusion coefficient adopted here is derived from the equation (3.1.2) with K_o and K^* set equal to 2.5×10^5 cm^2 sec^{-1} and 6×10^6 cm^2 sec^{-1} respectively. The boundary condition on the O_2 mixing ratio at the cloud tops was set equal to 1×10^{-7}.

The carbon and oxygen budget for the Venus atmosphere is illustrated in Figure 3. Photolysis of CO_2 produces 1.5×10^{13} molecules cm^{-2} sec^{-1} of carbon monoxide and an equal amount of atomic oxygen. Catalytic recombination above the cloud layer returns 0.65×10^{13} molecules cm^{-2} sec^{-1} of CO_2. Carbon monoxide is catalytically converted into CO_2 through the two major paths summarized by the net reactions (2.2.4) and (2.2.5). The excess CO and O (0.85×10^{13} cm^{-2} sec^{-1}) will be transported below the cloud deck and recombined by unidentified chemistry, providing an upward flux of CO_2 to complete the carbon and oxygen cycles.

The concentrations of key species calculated here differ from those of Sze and McElroy (1975) mainly because of revision

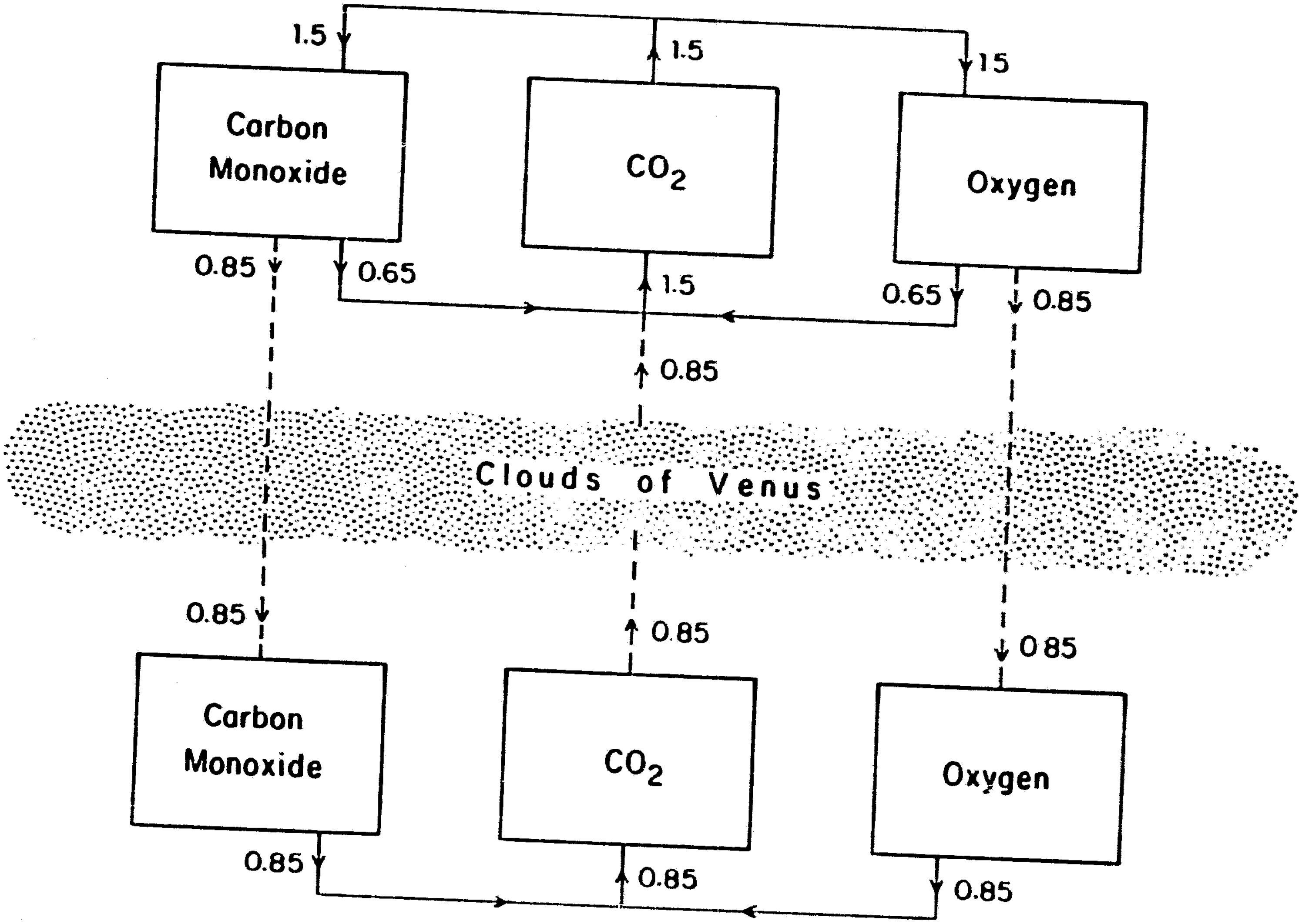

Figure 3.

Carbon and Oxygen Budget for Venus. The budgets are calculated using pre-sodium chemistry as described in the text.

in rate constants. In regions near the cloud top, the OH concentration, for instance, is about a factor of 4 to 5 lower than that calculated previously. The HO_2 concentration is reduced by about a factor of 2, whereas the O and O_2 concentrations are enhanced by factors of about 3 and 2 respectively. The increase in O and O_2 abundances is caused by the reduction of odd hydrogen which results primarily from the larger rate constant for the reaction (2.2.9) as discussed in Section 2.2. The net efficiency for CO_2 catalytic recombination, however, is reduced by only a factor of 2 because the updated rate constant for the key reaction

$$CO + OH \rightarrow CO_2 + H \qquad (4.1.1)$$

is about two times larger.

4.2 Sulfur Chemistry

The chemical model for the sulfur species (COS, S, SO, SO_2, SO_3, H_2SO_4) is given in Table 4. The photolysis of COS represents the sole source of sulfur considered in the present study. The source strength of sulfur is determined uniquely by the mixing ratio of COS at the cloud tops, for a given profile of the eddy diffusion coefficient. For the eddy diffusion coefficient specified in Section 4.1., photolysis of COS results in an integrated source for S of about 1×10^{12} cm^{-2} sec^{-1} for a COS mixing ratio of 10^{-7} at the cloud top. Higher values for the eddy diffusion coefficient would result in a larger source of sulfur.

The sulfur atom released from COS photolysis will participate in a rapid reaction with O_2

$$S + O_2 \rightarrow SO + O , \qquad (4.2.1)$$

forming SO and O. This represents a significant source for atomic oxygen near the cloud top as illustrated earlier in Figure 2.

Figure 4 shows the impact of sulfur chemistry on the key radial species O, OH and HO_2. The abundance of atomic oxygen below 68 km is significantly enhanced due to reaction (4.2.1). The increase in O concentration results in a reduction of HO_2 through the reaction

$$O + HO_2 \rightarrow OH + O_2 \qquad (4.2.2)$$

It follows that formation H_2O_2 through the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (4.2.3)$$

is suppressed significantly, resulting in a lesser production of OH through photolysis of H_2O_2.

Figure 5 shows the distribution of the sulfur species. Carbonyl sulfide (COS) is the dominant sulfur species below 65 km with SO_2 comparable to COS above this altitude. The abundances of the other sulfur species (S, SO, SO_3) are considerably smaller.

The formation of SO_2 is summarized in Figure 6. The dominant reaction is given by

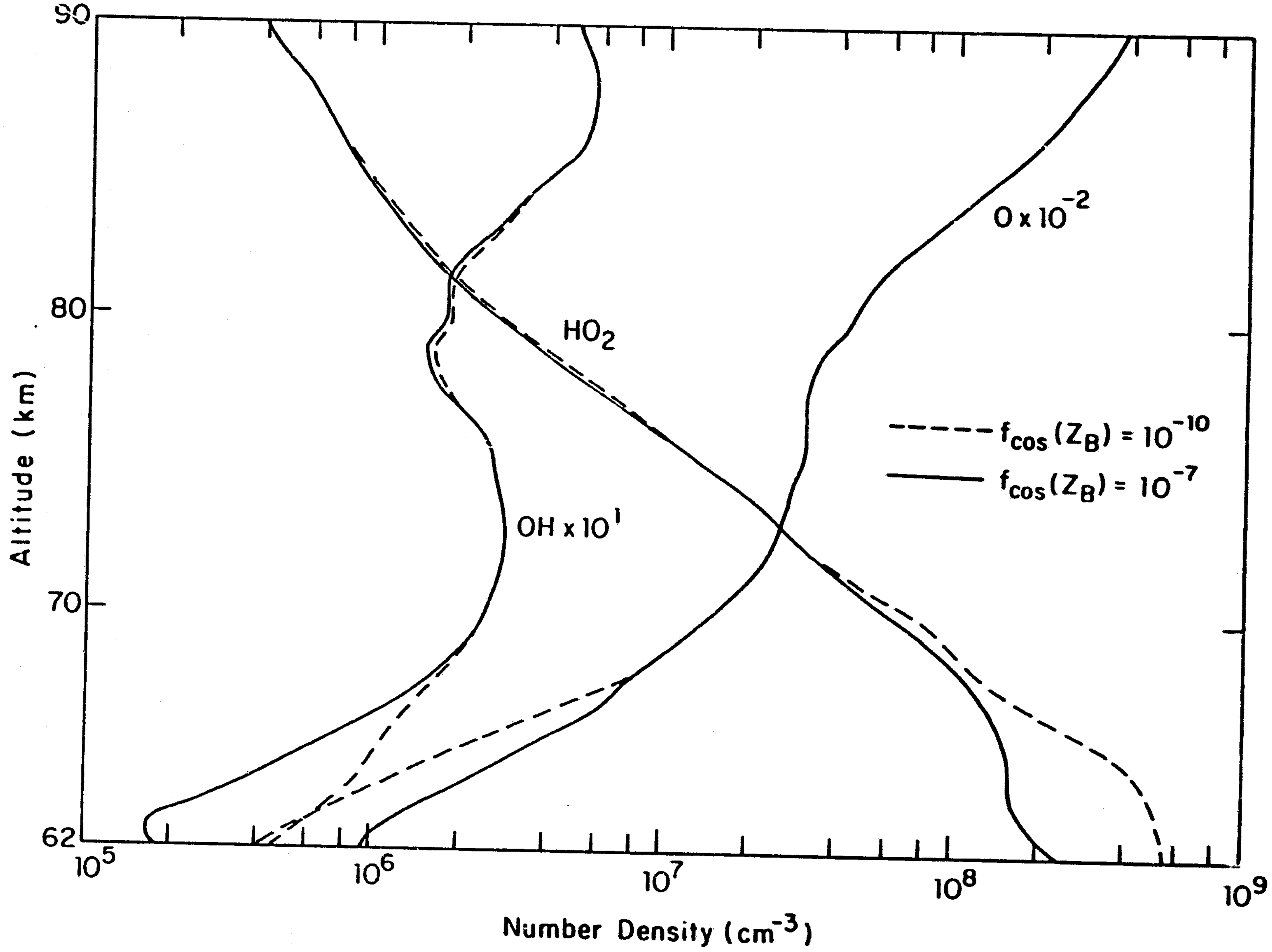

Figure 4.

Impact of Sulfur Chemistry on the Number Density Profiles of O, OH and HO_2. The mixing ratio of O_2 at the cloud top was set equal to 4×10^{-8}.

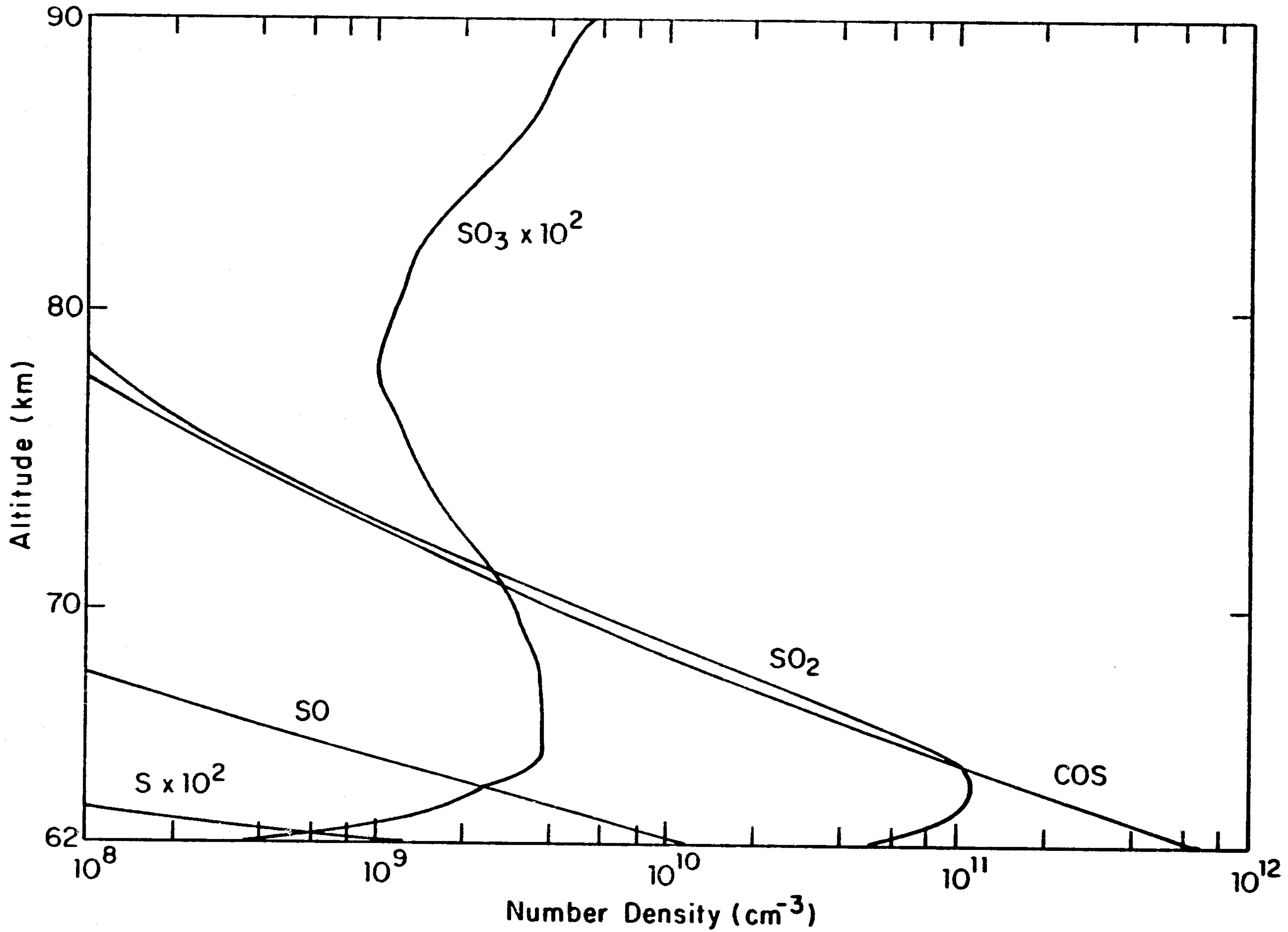

Figure 5
Concentration of Sulfur Species. The number densities were calculated assuming a mixing ratio for COS and O_2 at the lower boundary of 1×10^{-7} and 4×10^{-8} respectively.

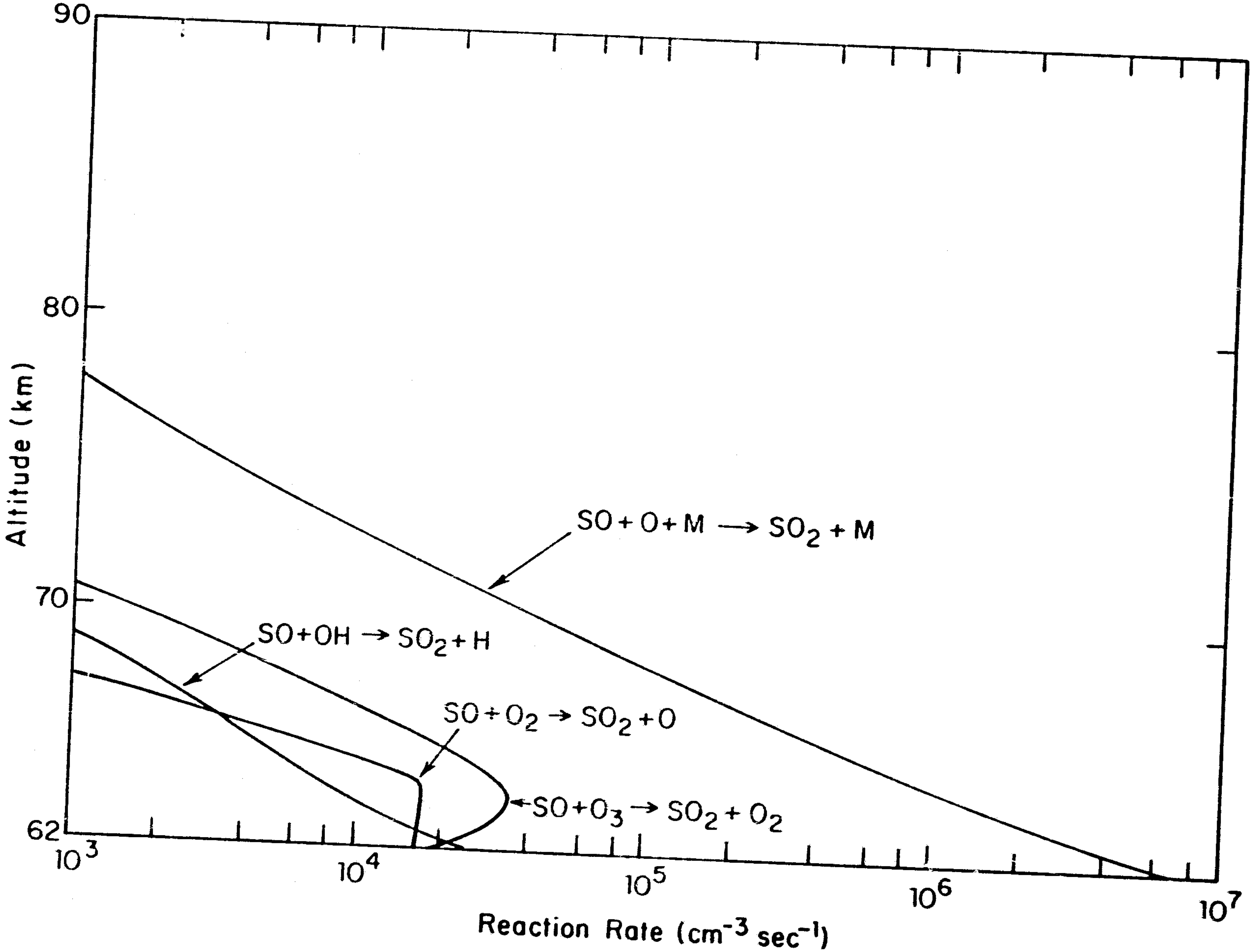

Figure 6

Production Rate for SO_2. The altitude dependence of each production rate was calculated using the COS and O_2 mixing ratios specified in Figure 5.

$$SO + O + M \rightarrow SO_2 + M \qquad (4.2.4)$$

which is an order of magnitude larger than reactions such as

$$SO + O_3 \rightarrow SO_2 + O_2 \qquad (4.2.5)$$

$$SO + O_2 \rightarrow SO_2 + O \qquad (4.2.6)$$

$$SO + OH \rightarrow SO_2 + H \qquad (4.2.7)$$

Reaction (4.2.7) was thought by Prinn (1973, 1975) to be the dominant reaction in the formation of SO_2.

Figure 7 shows the production rate of SO_3, which is equivalent to the production rate of H_2SO_4 molecules, as a function of altitude. The reaction

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (4.2.8)$$

provides the dominant source of SO_3 and is about two orders of magnitude larger than the source derived from reaction

$$SO_2 + HO_2 \rightarrow SO_3 + OH \qquad (4.2.9)$$

The reaction (4.2.9) was emphasized by Prinn (1973, 1975).

It appears that the overall reaction scheme for H_2SO_4 formation is represented by the reaction sequence (2.3.3) discussed in Section (2.3). This is essentially a sulfur and oxygen scheme in which odd hydrogen species are not directly involved.

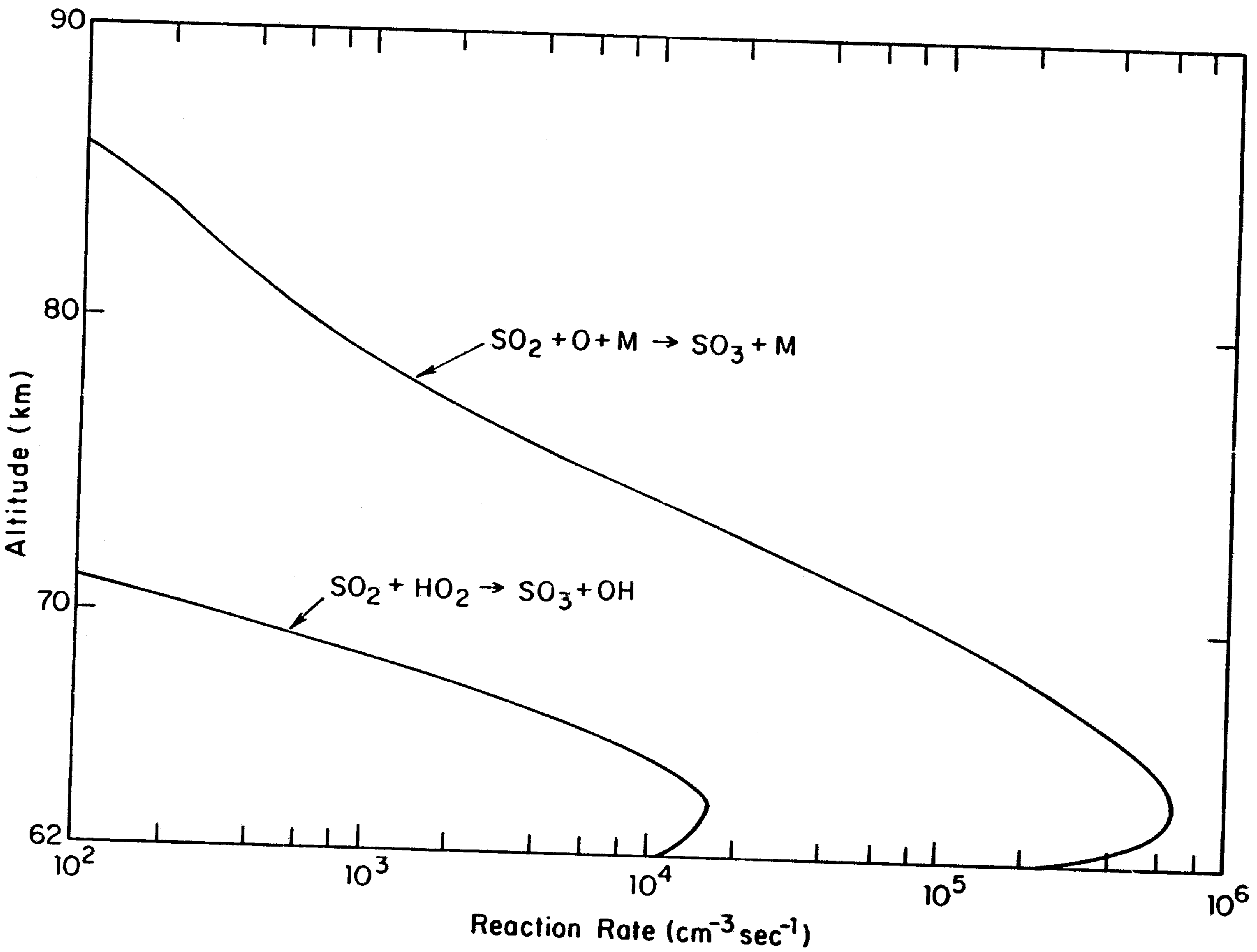

Figure 7
Production Rate for SO_3. Same description as in Figure 6.

One of the central issues in Venus aeronomy is understanding the fate of oxygen produced by CO_2 photolysis. There are four paths for oxygen to follow. It may be catalytically recombined with CO to form CO_2 as indicated by the net reaction schemes (2.2.4) and (2.2.5). Alternatively it may combine with sulfur forming SO_2 and H_2SO_4 both of which would be transported downward to replenish the Venus cloud. The remaining possibility is the formation of O_2 molecules which could also be tranported below the cloud deck.

Figure 8 describes the apportionment of oxygen between these four paths as a function of COS mixing ratio at the cloud top. At low concentrations of COS ($\sim 10^{-8}$(v/v)), catalytic recombination processes, X_{cat}, and a downward flux of O_2, X_{O_2}, consume almost all the available oxygen provided by photolysis of CO_2. At larger concentrations of COS ($\sim 10^{-7}$ (v/v)), X_{O_2} rapidly decreases with increasing COS. The fraction X_{cat}, however, decreases only slightly. The decrease in X_{O_2} is balanced by a corresponding increase in the downward flux of SO_2 and H_2SO_4, described in Figure 8 by X_{SO_2} and $X_{H_2SO_4}$ respectively.

For this particular calculation, the O_2 flux is consumed above the cloud tops for a COS mixing ratio of about 4×10^{-7}. Ideally this optimizes the condition for formation of H_2SO_4. However, it may also lead to an SO_2 abundance exceeding the observed upper limit. Computed values for X_{cat}, X_{O_2}, X_{SO_2} and

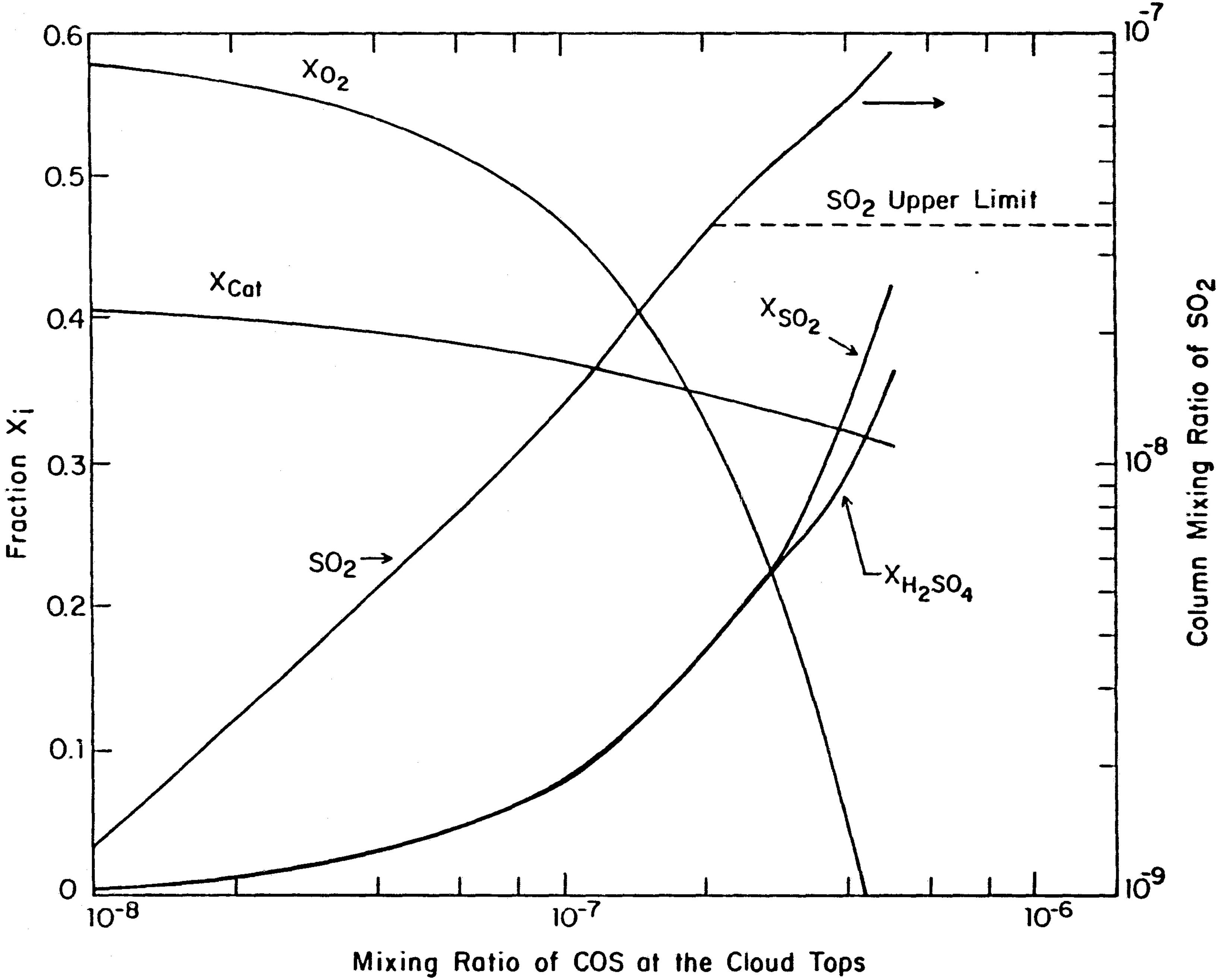

Figure 8
Impact of Sulfur on Oxygen Produced by CO_2 Photolysis. The dependence of the functions X_i (see the text) and the colunm density of SO2 on the abundance of COS is calculated for an O_2 mixing ratio of 4 x 10^{-7} at the cloud tops.

H_2SO_4 as a function of COS mixing ratio are given in Table 8. Flux ratios of interest, evaluated at the cloud tops, are also presented as a function of the COS mixing ratio in Table 9.

Given a downward flux of H_2SO_4 from the model calculation, the key question is how thick a cloud deck can be maintained under steady state conditions. Clearly the cloud abundance, N_c, would be in part determined by the downward flux of H_2SO_4, $\phi_{H_2SO_4}$, and in part determined by the residence time, τ, of the H_2SO_4 droplets in the cloud. The relationship between the three quantities N_c, $\phi_{H_2SO_4}$ and τ is given in Appendix A. The concentration of H_2SO_4 in the cloud deck is assumed to have a mixing ratio of 10^{-5} as suggested by Rossow and Sagan (1975). We consider two different cloud thicknesses of 5 and 10 km and show in Figure 9 the relationship between $\phi_{H_2SO_4}$ and τ . The residence time of the H_2SO_4 droplets is unknown, but is likely to lie between 0.5 and 3 years as indicated by the shaded area.

For large τ , about 3 years, a H_2SO_4 cloud as big as 10 km may be maintained by a COS mixing ratio as low as about 2×10^{-7}. on the other hand, if the residence time is as small as 0.5 year or less, an exceeding large concentration of COS, approaching 10^{-6}, is required to maintain a 10 km thick cloud. However, there are additional constraints on the abundance of COS. The oxygen flux will be exhausted by sulfur species when the COS mixing ratio exceeds about 5×10^{-7}. In addition the calculated SO_2 column

Table 8

Fate of Oxygen Atoms Produced by CO_2 Photolysis

$f_{COS}(Z_B)$	X_{cat}	X_{O_2}	X_{SO_2}	$X_{H_2SO_4}$
1×10^{-8}	.405	.577	.008	.010
1×10^{-7}	.370	.468	.080	.082
3×10^{-7}	.331	.189	.241	.239
4×10^{-7}	.321	.047	.340	.292
5×10^{-7}	.310	-.098	.424	.364

Table 9

Ratio of Fluxes at the Cloud Tops

$f_{COS}(z_B)$	$\frac{\phi_{O_2}}{\phi_{COS}}$	$\frac{\phi_{SO_2}}{\phi_{COS}}$	$\frac{\phi_{H_2SO_4}}{\phi_{COS}}$	$\frac{\phi_{H_2O}}{\phi_{COS}}$	$\frac{\phi_{H_2}}{\phi_{COS}}$	$\frac{\phi_{CO_2}}{\phi_{COS}}$	$\frac{\phi_{CO}}{\phi_{COS}}$
1×10^{-8}	-43.344	-.588	-.412	.178	.231	89.330	-90.330
1×10^{-7}	- 3.511	-.600	-.400	.368	.032	9.454	-10.454
3×10^{-7}	- 0.472	-.605	-.395	.383	.012	3.343	- 4.343
4×10^{-7}	- 0.089	-.637	-.363	.354	.009	2.542	- 3.542
5×10^{-7}	+ 0.147	-.637	-.363	.356	.007	2.067	- 3.067

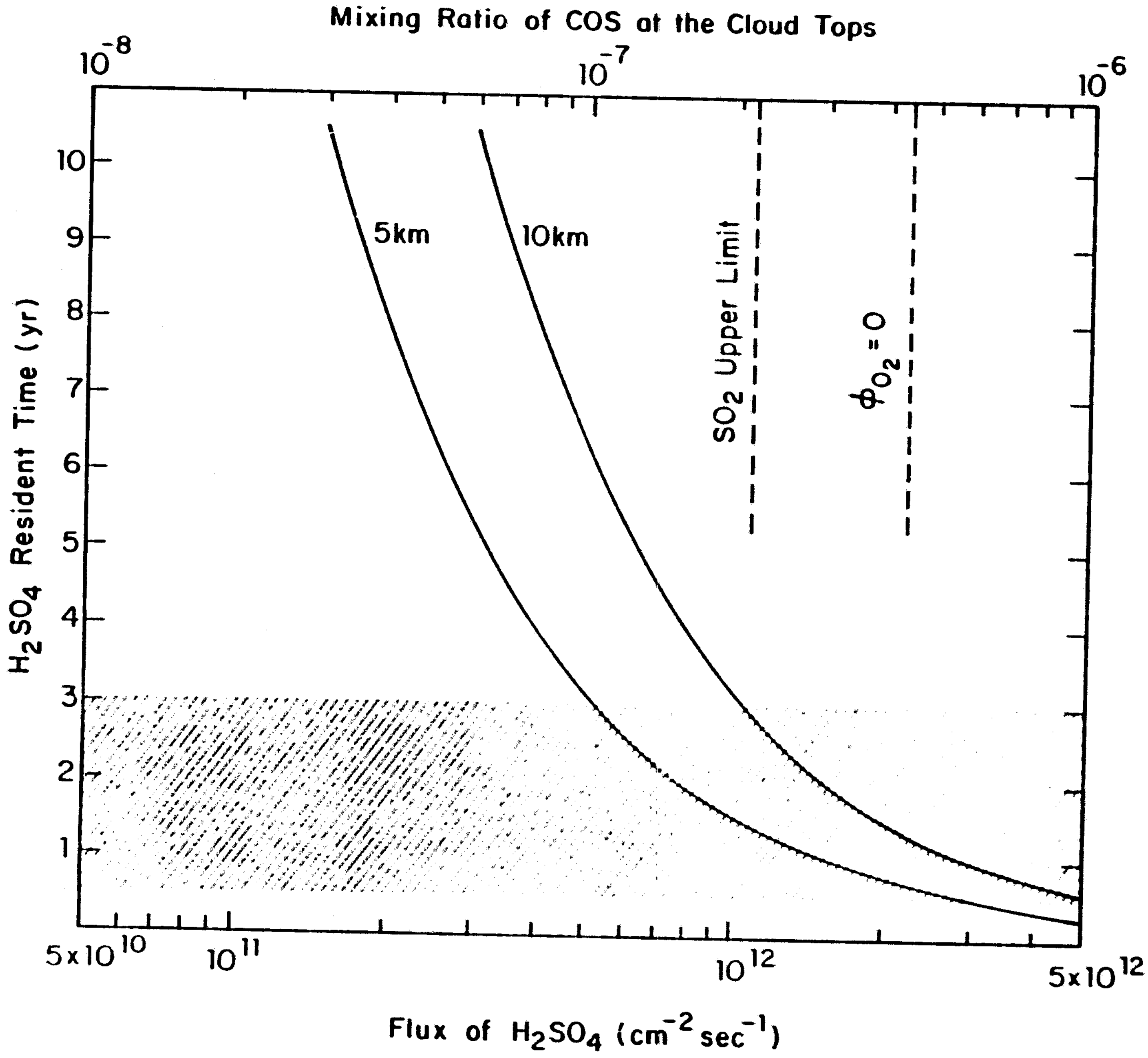

Figure 9
Formation of the H_2SO_4 Venus Cloud. The downward flux of H_2SO_4 to maintain a 5 km and 10 km thick cloud deck is shown as a function of resident time of H_2SO_4 molecules in the cloud, see text for discussion.

abundance might exceed the observed upper limit for a COS mixing ratio larger than about 2 x 10^{-7}. The calculated SO_2 column abundance is however highly model dependent and critically relies upon the assumed eddy diffusion coefficient and the adopted chemistry scheme. Revision in rate constants or diffusion coefficients or omission of key chemical reactions could modify the calculated distribution of sulfur species, particularly SO_2.

CHAPTER V

CONCLUDING REMARKS

We presented a model for Venus' atmosphere which complements and extends the earlier work by Prinn (1973, 1975) and by Sze and McElroy (1975). We assumed that sulfur is released by photolysis of COS (Prinn, 1973) and that oxygen is supplied by photolysis of CO_2. The supply rate for sulfur is determined by COS mixing ratio at cloud top and by dynamical processes. The oxygen supply rate, however, is influenced by a complex balance between odd hydrogen, sulfur and CO_2 photochemistry, in addition to transport processes.

We confirm the importance of O_2 as it controls the rate limiting step in the H_2SO_4 formation sequence. The presence of sulfur species may enhance the concentration of atomic oxygen above the cloud top due to the rapid reaction,

$$S + O_2 \rightarrow SO + O \qquad (5.1.1)$$

with S released from photolysis of COS. Subsequent reactions with atomic oxygen,

$$SO + O + M \rightarrow SO_2 + M \qquad (5.1.2)$$

and

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (5.1.3)$$

followed by

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (5.1.4)$$

appear to be the dominant processes for H_2SO_4 production.

Reaction scheme (2.3.2) which involves odd hydrogen species plays a relatively minor role in the formation of H_2SO_4 molecules. The calculated SO_2 abundance resulting from our present model appears to be quite high, but it could be lowered by using a faster rate constant for reaction (5.1.3) or by incorporating new reactions which transform SO_2 to SO_3 or H_2SO_4. Lower abundance of SO_2 would imply a more efficient scheme for H_2SO_4 production. Future measurements on SO_2 abundance would place an extremely useful contraint on Venus' sulfur chemical model.

For a given supply of H_2SO_4 molecules, the abundance of sulfuric acid cloud should be controlled by complex dynamic processes. We presented a steady state cloud model by introducing the concepts of residence or characteristic time constants for Venus' cloud deck. We showed that a 10 km cloud with a mean mixing ratio of $H_2SO_4 \approx 10^{-5}$ would require an extremely long residence time of about a few years. A short residence time (< 1 year) would imply either a less abundant H_2SO_4 cloud deck or a calculated flux of H_2SO_4 that is too low.

A significantly larger flux for H_2SO_4 than those calculated here would imply an alternate oxygen source for the oxidation of SO_2 molecules. An example of such an oxidation process is given by excited sulfur dioxide ($^1SO_2$, $^3SO_2$) chemistry, resulting from photo-excitation processes,

$$SO_2 + h\nu \rightarrow {}^1SO_2 \qquad (5.1.5)$$

and

$$SO_2 + h\nu \rightarrow {}^3SO_2 \qquad (5.1.6)$$

and might extract oxygen directly from CO_2 viz

$$CO_2 + {}^1SO_2 \rightarrow CO + SO_3 \qquad (5.1.7)$$

and

$$CO_2 + {}^3SO_2 \rightarrow CO + SO_3 \qquad (5.1.8)$$

Reaction scheme (5.1.5 - 5.1.8) would, in principle, bypass the limited supply of O_2. The potential role of excited sulfur chemistry in Venus' cloud formation will be investigated in our future work.

APPENDIX A

Relation Between COS Flux and Residence Time of H_2SO_4 Droplets for Different Cloud Thickness

For a steady state cloud, the rate of supply of H_2SO_4 molecules to the cloud deck by downward flux, $\phi_{H_2SO_4}$, must balance the rate of removal of H_2SO_4 cloud droplets which may be represented by

$$\left|\phi_{H_2SO_4}\right| = \frac{N_c}{\tau} \qquad (A.1)$$

where N_c is the column abundance of H_2SO_4 cloud and τ is the residence time or the characteristic time constant for the cloud deck.

The column density N_c depends upon the cloud thickness h, the average mixing ratio of H_2SO_4 in the cloud, $\bar{f}_{H_2SO_4}$, and the mean background concentration of CO_2, $\bar{n}_{CO_2}$, in the cloud deck :

$$N_c = \bar{f}_{H_2SO_4}\bar{n}_{CO_2}h \qquad (A.2)$$

Using the value 10^{-5} for $\bar{f}_{H_2SO_4}$, taken from Table 2, and a value of 1×10^{19} cm^{-3} for $\bar{n}_{CO_2}$,

$$N_c = 1 \times 10^{14} h^{*} \qquad (A.3)$$

where N_c has units of cm^{-2} and h^* is the cloud thickness expressed in km.

The expression (A.1) may alternatively be written as a relation between τ and the mixing ratio of COS at the cloud tops, $f_{COS}(Z_B)$. The flux of H_2SO_4 at the cloud tops is given by

$$\phi_{H_2SO_4} = -(1-\alpha)\ \phi_{COS}(Z_B) \qquad (A.4)$$

as discussed in Section 3.4. Furthermore the flux of COS at the cloud tops, $\phi_{COS}(Z_B)$, is determined uniquely by $f_{COS}(Z_B)$ for a given eddy diffusion profile. Using the eddy diffusion coefficient defined by (3.1.2) with K_o and K^* set equal to $2.5 \times 10^5\ cm^2\ sec^{-1}$ and $6 \times 10^6\ cm^2\ sec^{-1}$, respectively, we have

$$\phi_{COS}(Z_B) \approx 1 \times 10^{19}\ f_{COS}(Z_B) \qquad (A.5)$$

where $\phi_{COS}(Z_B)$ is expressed in units of $cm^{-2}sec^{-1}$. Combining (A.1), (A.3), (A.4) and (A.5), the desired relationship is

$$f_{COS}(Z_B)\ \tau = \frac{h^*}{(1-\alpha)} \qquad (A.6)$$

where τ is expressed in seconds. Assuming a representative value for α of 0.5 and values of 5 km and 10 km for h^*, the results presented in Figure 9 were calculated from (A.1), (A.3) and (A.6).

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