

# Atmospheric Composition, Chemistry, and Clouds

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Venus' atmosphere has a rich chemistry involving interactions among sulfur, chlorine, nitrogen, hydrogen, and oxygen radicals. The chemical regimes in the atmosphere range from ion-neutral reactions in the ionosphere to photochemistry in the middle atmosphere to thermal equilibrium chemistry and surface-atmosphere reactions in the lower atmosphere. This variety makes Venus an important planet to understand within the context of terrestrial-like planets, both in our own solar system and outside it. The primary chemical cycles are believed known but surprisingly few details about these cycles have been fully verified by concurrence among observations, experiments, and modeling. Good models have been developed that account for many properties of the cloud layers, but the size distribution, shape, and composition of the majority of the aerosol mass are still open issues. This chapter reviews the state of knowledge prior to the Venus Express mission for the composition, chemistry, and clouds of the neutral atmosphere on Venus. Observations by instruments on Venus Express, in combination with ground-based observations, laboratory experiments, and numerical modeling, should answer some of the major open questions regarding the composition, chemistry, and clouds of Venus' atmosphere.

## 1. INTRODUCTION

Interest in the composition of Venus' atmosphere began as early as Lomonosov's report from observations of the 1761 transit that Venus had an atmosphere and the pro-

posal that there were clouds in the atmosphere [*Huggins and Miller, 1864*]. In the latter half of the 20th century, numerous space missions and extensive ground-based telescopic observations provided significant insight into the composition and chemistry of Venus' atmosphere. The most intense study of Venus' photochemistry was in the decade from the early 1970's to the mid-1980's when the modern understanding of Earth's stratospheric chemistry also was being derived. Indeed, much of the chlorine and

sulfur chemistry identified in Earth's stratosphere was first proposed in early models of Venus' photochemistry [Prinn, 1985]. Photochemical modeling has had a renewed burst of interest since 2000. Throughout the 1980's and 1990's, and continuing to the present, ground-based observations showed that the abundances of trace species, intensity of airglow emission, temperatures, and wind velocities could vary markedly on timescales from hours to years. This variability has introduced a new dimension, time, into our understanding of chemistry in Venus' atmosphere, but few modeling studies have tackled this aspect and major uncertainties still surround the basic chemical state of the atmosphere. Observational advances in the last 20 years enabled retrieval of cloud characteristics and trace species abundances, many for the first time, from the base of the upper cloud layer to the lowest scale height above the surface. The resurgence of interest in the chemistry of Venus' atmosphere since 2000 has brought together advances from experimental measurements, ground-based observations, and numerical modeling. This chapter reviews the current state of knowledge of the chemistry of Venus' atmosphere (prior to the Venus Express mission), outlines current uncertainties, provides recommendations of future directions for research, and compares Venus' atmospheric chemistry to that of other terrestrial-like planets.

Venus' atmosphere can be divided into regions based on its composition, chemistry, and clouds. The upper atmosphere, above  $\sim 110$  km, has low densities and overlaps with the ionosphere so that photodissociation, ion-neutral, and ion-ion reactions are increasingly dominant as one goes to higher altitudes. The middle atmosphere,  $\sim 60$ – $110$  km, receives sufficiently intense ultraviolet (UV) radiation from the sun that its chemistry is dominated by photon-driven processes, termed "photochemistry." The lower atmosphere, below  $\sim 60$  km, receives little UV radiation from the sun, and due to the high atmospheric temperatures the chemistry is controlled increasingly by thermal processes, termed thermodynamic equilibrium chemistry or "thermochemistry," as one goes lower in the atmosphere. Bridging across the boundary between the lower and middle atmospheres are the cloud and haze layers which extend from  $\sim 30$ – $90$  km with the main cloud deck lying at  $\sim 45$ – $70$  km. The clouds define a transition region that reflects the competition between the middle atmosphere, dominated by photochemistry, and the lower atmosphere, dominated by thermochemistry [Esposito *et al.*, 1997]. This region is also where lightning could occur and produce NO [Krasnopolsky, 2006a] and where heterogeneous chemistry on aerosol and cloud particle surfaces may be important [Mills *et al.*, 2006]. Finally, the lowest scale height of the atmosphere is the region where surface-atmosphere interactions may dominate.

Three dominant chemical processes have been identified in the Venus atmosphere, which we will term the CO<sub>2</sub> cycle, the sulfur oxidation cycle, and the polysulfur cycle. The CO<sub>2</sub> cycle includes the photodissociation of CO<sub>2</sub> on the day side, transport of a significant fraction of the CO and O to the night side, production of O<sub>2</sub>, emission of highly variable oxygen airglow on both the day and night sides, and conversion of CO and O<sub>2</sub> into CO<sub>2</sub> via catalytic processes. The sulfur oxidation cycle involves the upward transport of SO<sub>2</sub>, oxidation of a significant fraction of the SO<sub>2</sub> to form H<sub>2</sub>SO<sub>4</sub>, condensation of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O to form a majority of the mass comprising the cloud and haze layers, downward transport of sulfuric acid in the form of cloud droplets, evaporation of the cloud droplets, and decomposition of H<sub>2</sub>SO<sub>4</sub> to produce SO<sub>2</sub>. There is solid observational evidence for both the CO<sub>2</sub> and the sulfur oxidation cycles. The polysulfur cycle is more speculative but plausible based on existing laboratory data and limited observations. It involves the upward transport of sulfur as either SO<sub>2</sub> or OCS, photodissociation to produce S, formation of polysulfur (S<sub>x</sub>) via a series of association reactions, downward transport of S<sub>x</sub>, thermal decomposition of S<sub>x</sub>, and reactions with oxygen and CO to produce SO<sub>2</sub> and OCS, respectively. Each of the cycles involves a number of trace species, such as ClO<sub>x</sub>, HO<sub>x</sub>, NO<sub>x</sub>, and SO<sub>x</sub>. The three cycles may (and probably do) interact through these trace species; see Plate 1. The strength of these links between the cycles in existing models depends on parameters that have significant uncertainties and few constraints from direct observational evidence.

The first part of this chapter summarizes recently published observations of the composition of Venus' atmosphere. The second and third parts discuss sulfur chemistry and the cloud layers, respectively, including the sulfur oxidation and polysulfur cycles. The fourth part discusses the chlorine chemistry that is believed to control the CO<sub>2</sub> cycle. The final sections discuss linkages among the chemical cycles, comparisons to other terrestrial-type planets, and recommendations for future research.

## 2. SUMMARY OF OBSERVATIONS AND RECENT DEVELOPMENTS

### 2.1 *Venera 15 Infrared Spectra: Observational Results and Interpretation*

VENERA 15 observed mainly the northern hemisphere, except for one orbital session when the spacecraft's orientation was changed to obtain a few tens of spectra in the equatorial region and southern midlatitudes. Absorption bands of three atmospheric gases (CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>) and also

H<sub>2</sub>SO<sub>4</sub> aerosols are clearly visible. The very strong 15 μm CO<sub>2</sub> band has different morphology at different locations, mostly owing to variability of the temperature profiles. Band center emission arises from atmospheric layers at about 90 km altitude. Differences appearing in the continuum likely reflect variability in the vertical structure of the upper clouds and haze.

Interpretation of Fourier Spectrometer (FTS) data [Moroz *et al.*, 1985, 1986, 1990; Spankuch *et al.*, 1985, 1990; Zasova *et al.*, 1985, 1989, 1993; Schaefer *et al.*, 1987, 1990; Linkin *et al.*, 1985; Ignatiev *et al.*, 1999; Koukouli *et al.*, 2005] gives the following results:

- (1) Upper cloud and upper haze particles consist of sulfuric acid water solutions, confirmed by the good agreement of synthetic and observed spectra.
- (2) The particle size distribution corresponds to the measured “mode 2” from the Pioneer Venus cloud particle size spectrometer (LCPS), with parameters as proposed by Pollack *et al.* [1980]. That is, a log-normal distribution with mean cross-section weighted size  $r = 1.05 \mu\text{m}$  and variance  $\sigma = 1.21$ . Possibly some other size distributions could also successfully match the data.
- (3) CO<sub>2</sub> pure gas transmission functions for a set of channels within the 15 μm band and computed aerosol transmission functions allow an iterative procedure (e.g., using relaxation as by Zasova *et al.* [1989]) to simultaneously retrieve the temperature and aerosol profiles.
- (4) The retrieved temperature and aerosol profiles from step (3) yield synthetic spectra for the SO<sub>2</sub> and H<sub>2</sub>O bands, which allow derivation of their abundances. These abundances are in good agreement with SO<sub>2</sub> measured in the UV [Zasova *et al.*, 1993].
- (5) The mean H<sub>2</sub>O abundance was  $12 \pm 5$  ppm with only a slight enhancement at equatorial latitudes and no clear day-night distinction [Koukouli *et al.*, 2005].

## 2.2. Water Vapor Measurements

Observed water vapor abundances in the middle atmosphere of Venus have shown strong variability—both spatially and temporally. The variability does not result from differences in retrieval technique or spectroscopic data [Koukouli *et al.*, 2005], and temporal variability in the absolute abundance and the spatial variations of the abundance has been reported by multiple instruments [Barker, 1975; Koukouli *et al.*, 2005; Sandor and Clancy, 2005] so both seem likely to be real.

In the lower atmosphere, spectra obtained by the entry probes on Venera 11, 13, and 14 were reanalyzed [Ignatiev *et al.*, 1997] using high temperature spectroscopic databases and a line-by-line radiative transfer code to assess

the previously reported inconsistencies between the results obtained from initial analyses of the Venera entry probe spectra [Moroz *et al.*, 1979, 1980; Moshkin *et al.*, 1983; Young *et al.*, 1984] and from ground-based observations of near-infrared emission from Venus’ nightside [Pollack *et al.*, 1993]. The new analyses by Ignatiev *et al.* [1997] found results that are very similar to those derived from ground-based observations by Pollack *et al.* [1993]. Ignatiev *et al.* [1997] concluded the H<sub>2</sub>O mixing ratio at 10–48 km was either close to a constant value of  $30 \pm 10$  ppm or has a weak minimum at 10–20 km. In the clouds, they found the H<sub>2</sub>O mixing ratio was in the range 30–50 ppm and below 5 km altitude, the mixing ratio for H<sub>2</sub>O probably increases to 50–70 ppm. Ignatiev *et al.* [1997] also concluded that the much larger mixing ratios determined by in situ experiments on the Venera entry probes are not likely to be reliable.

## 2.3. Sulfur Dioxide Measurements

SO<sub>2</sub> was first detected in the atmosphere of Venus by Barker [1979] from the ground, and it was subsequently confirmed by Stewart *et al.* [1979] and Conway *et al.* [1979]. These observations indicated that the abundances of SO<sub>2</sub> in the 1978–1979 period were larger than the previously established upper limits [Owen and Sagan, 1972] by orders of magnitude. Continuous observations by Pioneer Venus from 1978 to 1986 show a steady decline in the cloud top SO<sub>2</sub> abundance toward values consistent with previous upper limits [Esposito *et al.*, 1988]. This decline has been confirmed by International Ultraviolet Explorer (IUE) observations [Na *et al.*, 1990] and by Hubble observations [Na and Esposito, 1995], see Plate 2 and Figure 1. Analysis of UV spectra from the Hubble Space Telescope (HST) Goddard High Resolution Spectrometer (GHRS) gives an SO<sub>2</sub> abundance of less than 25 ppb at the cloud tops [Na and Esposito, 1996]. See Figure 1 for the time history of SO<sub>2</sub> cloud top measurements. Explanations that have been advanced for the likely rapid increase and observed slow decline of SO<sub>2</sub> include active volcanism [Esposito, 1984], changes in the effective eddy diffusion within the cloud layers [Krasnopolsky, 1986, p. 147], and changes in atmospheric dynamics [Clancy and Muhleman, 1991]. It is important to note that the volcano hypothesis uses the volcanic eruption as a source of buoyancy that allows the abundant SO<sub>2</sub> below the Venus clouds to break through the stable upper cloud layer. The entrained SO<sub>2</sub> is then observable remotely at the cloud top in the UV. Similarly, because the observed SO<sub>2</sub> mixing ratio may differ by as much as four orders of magnitude from the base to the top of the cloud layers [Berteaux *et al.*, 1996; Esposito *et al.*, 1997], a small change in the effective eddy diffusion within the cloud layers may significantly alter the cloud top

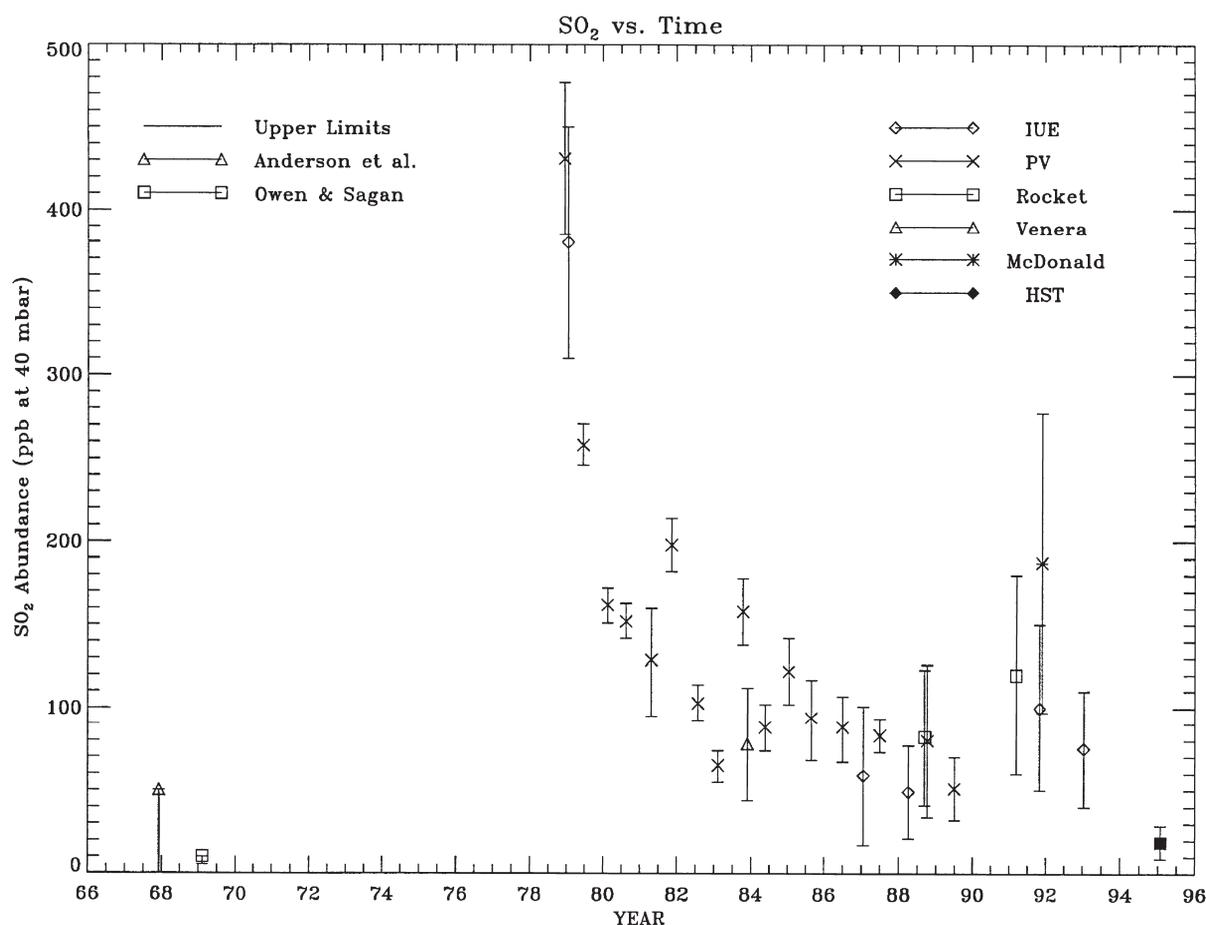


Figure 1. SO<sub>2</sub> abundance near the Venus cloud tops. (From *Esposito et al.*, 1997)

abundance of SO<sub>2</sub> [Krasnopolsky, 1986, p. 147]. The SO<sub>2</sub> abundance below the clouds varies much more slowly, related to the amount of volcanic activity over geologic time scales of millions of years. See *Fegley et al.* [1997a].

The observed rate of change in the cloud top abundance of SO<sub>2</sub> is significantly slower than would be expected if the change were due entirely to photochemical processes. The photochemical lifetime of SO<sub>2</sub> at 68–70 km altitude is about  $3 \times 10^3$  s, but SO<sub>2</sub> is rapidly produced again from SO, so the time scale for net loss of SO<sub>2</sub> via oxidation to SO<sub>3</sub> is much longer,  $10^6$ – $10^7$  s [Winick and Stewart, 1980; Krasnopolsky and Pollack, 1994; Pernice et al., 2004], which is comparable to or longer than the  $1$ – $2 \times 10^6$  s time scale for vertical transport due to eddy diffusion in models [Mills, 1999a]. The photochemical lifetime against oxidation to SO<sub>3</sub> depends on the column abundance of SO<sub>2</sub> and the production rate for SO<sub>3</sub>, both of which have uncertainties.

The changes in SO<sub>2</sub> above and within the clouds of Venus may have a significant effect on the photochemistry of the clouds of Venus. Pioneer Venus observations have shown that

the clouds of Venus are created by the photochemical processes that oxidize upwelling SO<sub>2</sub> [Winick and Stewart, 1980; Krasnopolsky and Parshev, 1981abc; 1983; Yung and DeMore, 1981; 1982]. Thus any significant changes in SO<sub>2</sub> may have an effect on the chemistry and dynamics of the clouds.

#### 2.4. Clouds and Hazes

VENERA-15 FS spectra provided a strong confirmation of aqueous solution (75–85%) of sulfuric acid as the particulate material in the upper clouds. Otherwise, such good coincidence of synthetic and observed spectra would be impossible. The first *in situ* detection of sulfuric acid was made in experiments SIGMA-3, a gas chromatograph, and MALAHIT, a mass spectrometer. The analysis of SIGMA-3 results yields the average mass loading of sulfuric acid about  $1 \text{ mg/m}^3$ , estimated for heights 48–54 km and “much lower” at about 54 km [Porshnev et al., 1987]. Conclusions from MALAHIT analysis are even less definite and not in a good agreement with SIGMA-3 results; they give an average mass

loading between 2 and 10 mg/m<sup>3</sup> [Surkov *et al.*, 1987]. Both experiments can say nothing about the upper cloud.

Very interesting, but puzzling, results were obtained by elemental X-ray analysis of the thin layers collected by the IPF experiment [Andreichikov *et al.*, 1987], which was an aerosol analyzer on VEGA. Three elements were identified: sulfur, chlorine and phosphorus. Sulfur and chlorine in cloud particles had been detected previously by similar measurements, but not phosphorus. It is clear that some P-bearing substance can be important as a particulate in lower clouds. Phosphoric acid H<sub>3</sub>PO<sub>4</sub> is a likely candidate for this substance and phosphorous anhydride P<sub>4</sub>O<sub>6</sub> may be the gas responsible for its production [Andreichikov, 1987]. A critical review of these data was given by Krasnopolsky [1989]. The key conclusion in the paper is that the lower subcloud boundary at the level about 33 km registered on VENERA 8 and later on some other missions can be explained by phosphoric acid particles dominating in the subclouds. The refractive index 1.7 estimated for some of the particles registered in ISAV-A experiment can be understood if they are sulfur. Some evidence for the presence of sulfur aerosols in clouds is also found in the analysis of the SIGMA-3 and IPF results.

### 2.5. Ground-Based Observations of the Lower Atmosphere

Important new information from near IR measurements of the Venus nightside probes the deeper Venus atmosphere through windows in the CO<sub>2</sub> absorption spectrum. Discovery of nightside emissions at 1.7 and 2.3 μm on Venus by Allen and Crawford [1984] has been extremely important for further progress in study of the chemical composition. These emissions were readily identified [e.g., Krasnopolsky, 1986, p. 181] as spectral windows to the lower atmosphere. Later, windows at 1.31, 1.27, 1.18, and 1.01 μm were found, and lines of CO<sub>2</sub>, H<sub>2</sub>O, HDO, SO<sub>2</sub>, CO, OCS, HCl, and HF have been identified. Radiation in each window is formed at a particular altitude range, and by comparing data for the same species at different windows, it becomes possible to obtain vertical profiles. Furthermore, lines of different strengths were observed in the 2.3 μm window, and this allowed Pollack *et al.* [1993] to derive both the mixing ratio and its gradient.

Pollack *et al.* [1993] found the mixing ratio for HF was 1–5 ppb at 33.5 km with no evidence for a vertical gradient, HCl had a mixing ratio of 0.48 ± 0.12 ppm at 23.5 km with no evidence for a vertical gradient, and H<sub>2</sub>O had a constant mixing ratio of 30 ± 10 ppm at 10–40 km. The results for HF from Pollack *et al.* [1993], Young [1972], and Connes *et al.* [1967] suggest the mixing ratio for HF is approximately constant below the cloud tops. A more refined analysis of 1.7 μm spectra and earlier telescopic observations suggest

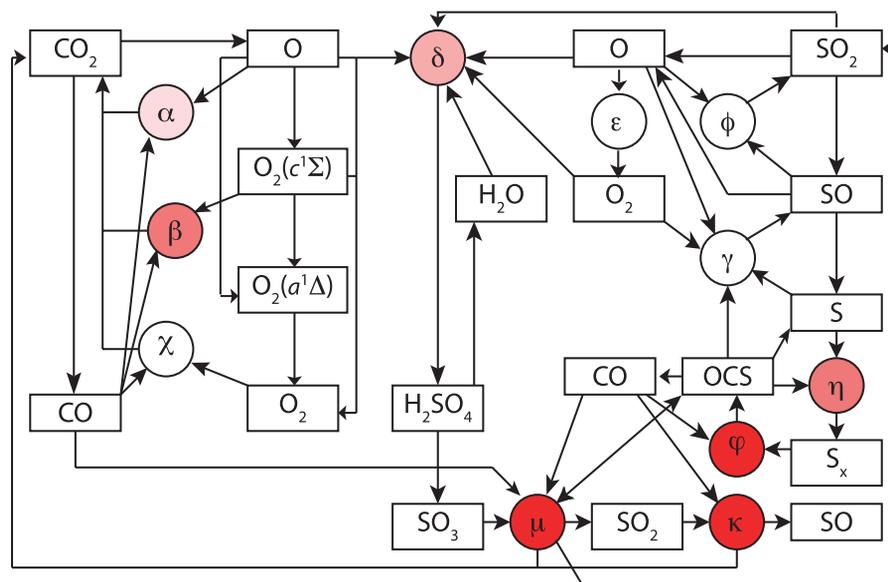
the mixing ratio of HCl decreases from 1.0 ppm near 5 km to 0.4 ppm at the cloud tops [Dalton *et al.*, 2000; Connes *et al.*, 1967; Young, 1972].

The currently recommended mixing ratio for H<sub>2</sub>O is 30 ± 10 at 15–45 km and 30 ± 15 at 0–15 km [Taylor *et al.*, 1997]. Other contemporaneous analyses [Ignatiev *et al.*, 1997; Meadows and Crisp, 1996] are roughly consistent with this recommendation (Plate 3), but H<sub>2</sub>O close to the surface is harder to constrain [de Bergh *et al.*, 2006].

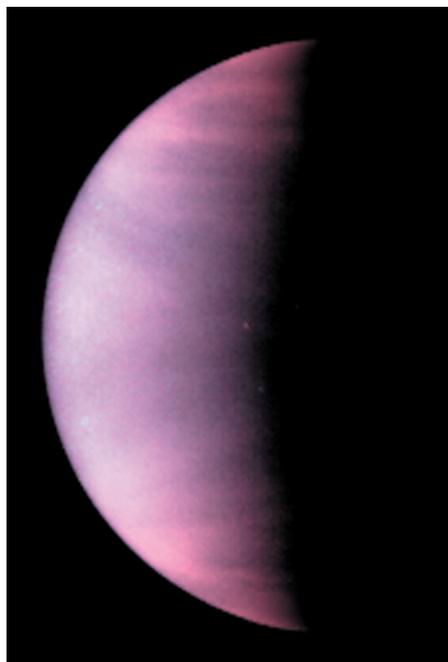
Pollack *et al.* [1993] also found the mixing ratios of CO and OCS were equal to 23 ± 5 and 4.4 ± 1 ppm at 36 and 33 km, respectively, with gradients of 1.2 ± 0.45 and -1.58 ± 0.3 ppm/km, respectively. Modeling by Krasnopolsky and Pollack [1994], Plate 3, agrees well with the retrieved mixing ratios and gradients for CO and OCS. In their modeling, OCS reacts with SO<sub>3</sub> to produce CO above ~ 33 km. Subsequent observations [Marcq *et al.*, 2005; 2006] found a global average CO mixing ratio of 24 ± 2 ppm at 36 km with a vertical gradient of 0.6 ± 0.3 ppm/km and a larger abundance of CO at 20–40° S latitude than at 0–20° S. Marcq *et al.* [2005; 2006] also found a global average OCS mixing ratio of 0.55 ± 0.15 ppm at 36 km with a vertical gradient of -0.28 ± 0.1 ppm/km and a smaller abundance of OCS at 20–40° S latitude than at 0–20° S. The newer observations of CO are quantitatively consistent with the earlier results where the observational altitudes agree, although the best fit vertical gradient for CO is a factor of two smaller in the newer results. The smaller gradient in CO mixing ratio from Marcq *et al.* [2005; 2006] is more consistent with measurements by instruments on Pioneer Venus and Venera 12 [Bezard and de Bergh, 2007] as shown in Plate 3. The best fit mixing ratio and the vertical gradient for OCS from the newer observations are a factor of eight and five, respectively, smaller than the earlier results. The gradients for CO and OCS in the newer results, however, are still approximately equal in magnitude and opposite in sign. Further, the spatial anticorrelation between CO and OCS mixing ratios observed by Marcq *et al.* [2005; 6] is qualitatively consistent with the anticorrelation in the vertical gradients of CO and OCS seen by Pollack *et al.* [1993] and Marcq *et al.* [2005; 6] and suggests conversion between CO and OCS, possibly due to surface buffering [Fegley and Treiman, 1992], thermochemical equilibrium chemistry [Krasnopolsky and Parshev, 1979], or kinetic conversion of OCS to CO<sub>2</sub> and CO [Krasnopolsky and Pollack, 1994].

### 2.6. Contemporaneous Reviews of Atmospheric Composition

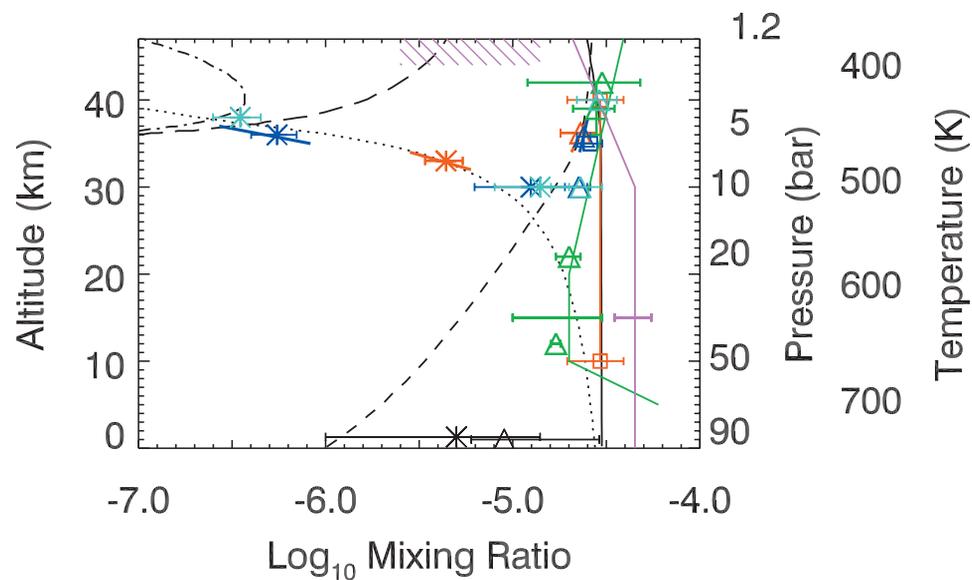
Two contemporaneous review articles provide additional details on observations that have been made of the chemical



**Plate 1.** Schematic diagram for the atmospheric chemistry on Venus. Catalytic schemes are indicated by the Greek letters in circles.  $\alpha$  = Schemes (E), (G1), (G2), (G3), and (N) in this chapter and the heterogeneous oxidation of CO on aerosols [Mills *et al.*, 2006].  $\beta$  = CO + O<sub>2</sub>(c) scheme [Slanger *et al.*, 2006; Mills *et al.*, 2006].  $\chi$  = Scheme (H) in this chapter and Schemes XIIab in Yung and DeMore [1982].  $\delta$  = Schemes (H) and (J) in this chapter and Schemes VIab and XIIab in Yung and DeMore [1982].  $\epsilon$  = Scheme (D).  $\phi$  = Reactions (6), (7), and (41).  $\gamma$  = Reactions (3), (4), and (5).  $\eta$  = Reactions (8), (9), and (17) and the chlorosulfane schemes in Mills and Allen [2007].  $\varphi$  = net Reaction (14).  $\mu$  = net Reactions (12) and (13), and Reactions (15) and (16).  $\kappa$  = Reaction (18). The catalytic schemes with white background have been confirmed by laboratory chemical kinetic studies. Those in shades of red have not been fully confirmed. The degree of laboratory confirmation is indicated by the lightness of the shade of red. The darkest red have received no confirmation in laboratory studies; those in light red are largely but not completely confirmed.



**Plate 2.** Venus image from HST at 218 nm. (Space Telescope Science Institute)



**Plate 3.** Predicted and observed composition of the lower atmosphere. Calculated abundances from a chemical kinetics model (model 1) [Krasnopolsky and Pollack, 1994] for H<sub>2</sub>O (solid black line), CO (short dashed black line), OCS (dotted black line), H<sub>2</sub>SO<sub>4</sub> (long dashed black line), and SO<sub>3</sub> (dash dotted black line). Calculated abundances from a thermochemical equilibrium model for the conditions believed to exist at the surface are shown for CO (black triangle) [Fegley *et al.*, 1997b] and OCS (black asterisk) [Hong and Fegley, 1997]. Retrieved H<sub>2</sub>O abundances are the magenta solid line [Meadows and Crisp, 1996], the green solid line [Ignatiev *et al.*, 1997], the red solid line with red squares [Pollack *et al.*, 1993], and the blue square [Marcq *et al.*, 2006]. In site measurements of CO are the green triangles [Gel'man *et al.*, 1979; Oyama *et al.*, 1980]. Retrieved CO abundances are the blue triangles [Marcq *et al.*, 2006] and the red triangle [Pollack *et al.*, 1993]. Retrieved OCS abundances are the blue asterisks [Marcq *et al.*, 2006] and the red asterisk [Pollack *et al.*, 1993]. The range of H<sub>2</sub>SO<sub>4</sub> vapor abundances retrieved from observations is indicated by the magenta hatched region [Bezard and de Bergh, 2007]. Recommended values [Taylor *et al.*, 1997] for CO are the cyan triangles and for OCS are the cyan asterisks.

composition of Venus' lower atmosphere [Bezard and de Bergh, 2007] and Venus' atmosphere below 100 km altitude [de Bergh et al., 2006].

### 3. SULFUR CHEMISTRY

Sulfur chemistry is critical to the composition of the Venus atmosphere, and four sulfur species have been firmly identified: SO<sub>2</sub>, SO, OCS, and H<sub>2</sub>SO<sub>4</sub> (vapor and in aerosols). Recently published measurements of their abundances are summarized in Table 1, Table 3, de Bergh et al. [2006], and Bezard and de Bergh [2007]. H<sub>2</sub>S was reported by Pioneer Venus below 20 km [Hoffman et al., 1980], but it was never confirmed by an independent measurement and the reported value is at least an order of magnitude larger than would be expected from thermochemical equilibrium calculations [Fegley et al., 1997b]. Strong absorption in spectrophotometer data from VENERA 11, 12, 13 and 14 at 450–600 nm between 10 and 30 km has been attributed most commonly to gaseous elemental sulfur (polysulfur, S<sub>x</sub>) [Moroz et al., 1979; Sanko, 1980; Krasnopolsky, 1987; Maiorov et al., 2005] and there is good agreement between calculated and observed Venera-11 spectra at 3–19 km assuming the abundance of S<sub>3</sub> increases with altitude from 0.03 ppbv at 3 km to 0.1 ppbv at 19 km [Maiorov et al., 2005]. Pollack et al. [1980] suggested

SO<sub>2</sub> could be at least partially responsible for the observed absorption at 400–500 nm below the cloud layers, but they did not publish the detailed results of their computations and no subsequent publication has either confirmed or refuted the importance of absorption by SO<sub>2</sub> below 40 km. The presence of thiozone (S<sub>3</sub>) and polysulfur (S<sub>x</sub>) in the clouds has been inferred [Porshnev et al., 1987], but there has not been a definitive detection of S<sub>x</sub> in the middle atmosphere.

The chemical scheme proposed by Prinn [1975, 1978, 1979] is based on a prediction by Lewis [1970] of sulfur species with mixing ratios of 60 ppm for OCS, 6 ppm for H<sub>2</sub>S, and 0.3 ppm for SO<sub>2</sub>. In the 1970s, sulfuric acid was clearly identified in the clouds [Hansen and Hovenier, 1974], while a search for gaseous sulfur components was not successful until 1979 (see Sec. (2.3)). Prinn [1975] suggested a scheme of photochemical formation of sulfuric acid from carbonyl sulfide OCS and later [Prinn, 1978] proposed the inverse processes leading to OCS and elemental sulfur from H<sub>2</sub>SO<sub>4</sub>. The predicted SO<sub>2</sub> mixing ratio was about a few ppm above 30 km and much larger than that near the surface. Prinn [1979] supposed that dissociation of S<sub>3</sub> and S<sub>4</sub> by the near ultraviolet ( $\lambda \approx 350$  nm) might produce hot sulfur atoms with energies close to 1.5–2.5 eV that could drive chemistry in the lower atmosphere by reacting with H<sub>2</sub>O and CO<sub>2</sub> to form SH, OH, SO, and CO. The UV photometer on the Venera 14

**Table 1.** Gas-phase species abundance observations published since 2000. †Sandor and Clancy [2005] observed HDO and assumed the above cloud D/H ratio was  $157 \pm 15$  times SMOW [Bjoraker et al. 1992] to obtain the quoted H<sub>2</sub>O abundances.

Species	Mixing Ratio (v/v)	Altitude	Year/Location	Notes
Cloud-top H <sub>2</sub> O	(10 ± 5)–(90 ± 15) ppm	~ 110–160 mbar (~ 62–64 km)	1978–1979	Koukouli et al. [2005]
Cloud-top H <sub>2</sub> O	~ 12 ± 5 ppm	~ 120–200 mbar (~ 60–64 km)	1983	Koukouli et al. [2005]
H <sub>2</sub> O (inferred from HDO <sup>†</sup> )	(0.0 ± 0.06)–(3.5 ± 0.3) ppm	65–100 km	1998–2004	Sandor and Clancy [2005]
SO <sub>2</sub>	430–10 ppb	40 mbar (~ 68 km)	1968–1995	See Figure 1
SO <sub>2</sub>	≤ 50 ppm	35–55	1996, polar regions	Jenkins et al. [2002]
SO <sub>2</sub>	≤ 100 ppm	35–55	1996, low latitudes	Jenkins et al. [2002]
SO <sub>2</sub>	≤ 50 ppm	Below lower cloud	1996, 1999	Butler et al. [2001]
H <sub>2</sub> SO <sub>4</sub> (g)	0–9 ppm	35–55	1996	Jenkins et al. [2002]
H <sub>2</sub> SO <sub>4</sub> (g)	1–30 ppm	47–58 km	1983–1984, mid to high latitudes	Gubenko et al. [2001]
H <sub>2</sub> SO <sub>4</sub> (g)	1–2.5 ppm	At and below lower cloud	1996, 1999	Butler et al. [2001]
HCl	1–0.4 ppm	5–70 km		Dalton et al. [2000]
NO	5.5 ± 1.5 ppb	≤ 60 km	2004	Krasnopolsky [2006a]
NO flux	(6 ± 2) × 10 <sup>7</sup> cm <sup>-2</sup> s <sup>-1</sup>		2004	Krasnopolsky [2006a]
S <sub>3</sub>	0.03–0.1 ppb	3–19 km	1978	Maiorov et al. [2005]
CO	2 × 10 <sup>-6</sup> –2 × 10 <sup>-4</sup>	10–90 km	2003–2004	Marcq et al. [2005]
OCS	2 × 10 <sup>-7</sup> –10 <sup>-5</sup>	20–48 km	2003–2004	Marcq et al. [2005]

**Table 2.** Airglow observations published since 2000.

Airglow Band	Intensity	Altitude	Year/Location	Notes
O ( <sup>1</sup> S – <sup>1</sup> D) 557.7 nm	(≤ 10) - 167 R	~ 100 km	1999, 2001, 2002	<i>Slanger et al.</i> [2006]
O ( <sup>1</sup> D – <sup>3</sup> P) 630 nm	< 20 R		1999	<i>Slanger et al.</i> [2001]
O <sub>2</sub> (c <sup>1</sup> Σ – X <sup>3</sup> Σ) Herzberg II	5.1 kR	mesosphere	1999	<i>Slanger et al.</i> [2001]
O <sub>2</sub> (c <sup>1</sup> Σ – X <sup>3</sup> Σ) Herzberg II	3.1 kR	mesosphere	2001	<i>Slanger et al.</i> [2006]
O <sub>2</sub> (A <sup>3</sup> Δ – a <sup>1</sup> Δ) Chamberlain	120 R	mesosphere	1999	<i>Slanger et al.</i> [2001]

**Table 3.** Cloud and haze observations published since 2000.

Observation	Value	Altitude	Year/Location	Notes
Cloud top pressure	5 – 30 mbar		1978 - 1991	<i>Braak et al.</i> [2002]
Cloud-top unit optical depth	110 – 160 mbar		1978 – 1979	<i>Koukouli et al.</i> [2005]
Cloud-top unit optical depth	120 – 200 mbar		1983	<i>Koukouli et al.</i> [2005]
Upper haze column abundance	0.25 – 1.5 μm <sup>-2</sup>	> cloud top	1978-1991	<i>Braak et al.</i> [2002]
H <sub>2</sub> SO <sub>4</sub> Droplet column abundance	15 cm <sup>-2</sup>	> cloud top	1999 - 2004	<i>Mallama et al.</i> [2006]
H <sub>2</sub> SO <sub>4</sub> Droplet diameter	2.1 μm	> cloud top	1999 - 2004	<i>Mallama et al.</i> [2006]

**Table 4.** Predicted gas-phase species which have not been observed in the middle atmosphere.

Predicted Species	Maximum Abundance	Altitude	Column Abundance	Notes
ClO	4 x 10 <sup>7</sup> cm <sup>-3</sup>	70 km	1 x 10 <sup>14</sup> cm <sup>-2</sup>	<i>Pernice et al.</i> [2004]
Cl <sub>2</sub>	6 x 10 <sup>10</sup> cm <sup>-3</sup>	60 km	6 x 10 <sup>16</sup> cm <sup>-2</sup>	<i>Pernice et al.</i> [2004]
ClC(O)OO	1 x 10 <sup>8</sup> cm <sup>-3</sup>	84 km	7 x 10 <sup>13</sup> cm <sup>-2</sup>	<i>Pernice et al.</i> [2004]
COCl <sub>2</sub>	4 x 10 <sup>8</sup> cm <sup>-3</sup>	66 km	7 x 10 <sup>14</sup> cm <sup>-2</sup>	<i>Pernice et al.</i> [2004]
ClSO <sub>2</sub>	3 x 10 <sup>10</sup> cm <sup>-3</sup>	58 km	6 x 10 <sup>15</sup> cm <sup>-2</sup>	<i>Pernice et al.</i> [2004]
S <sub>2</sub> O	1 x 10 <sup>10</sup> cm <sup>-3</sup>	64 km	2 x 10 <sup>15</sup> cm <sup>-2</sup>	<i>Na and Esposito</i> [1997]

lander, however, found that the intensity of NUV radiation (320–390 nm) decreased by a factor of ~ 7 between 60 and 48 km [*Ekonomov et al.*, 1983]. This suggests the sulfur atoms produced from photodissociation of S<sub>3</sub> and S<sub>4</sub> in the lower atmosphere would have energies below 0.5 eV, which may not be sufficient to drive all of the lower atmosphere reactions proposed by Prinn [*Krasnopolsky and Pollack*, 1994], although there may still be sufficient energy to drive Prinn's proposed reaction S + CO<sub>2</sub> → SO + CO.

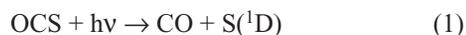
As noted above, there are two parts to the chemistry of sulfur species in the atmosphere of Venus. In the lower atmosphere and on the surface, the chemistry is dominated by thermodynamic equilibrium chemistry. Above the cloud

tops, the chemistry is driven by photochemistry. Thus, the partitioning of sulfur among the different species represents a competition between thermodynamic equilibrium chemistry in the lower atmosphere and photochemistry above the cloud tops. We first discuss the photochemistry of sulfur in the middle atmosphere and then the thermal equilibrium chemistry of sulfur in the lower atmosphere.

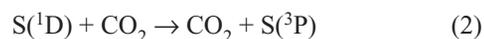
### 3.1. Sulfur Photochemistry

The primary sulfur species in the middle atmosphere is SO<sub>2</sub>, which undergoes either oxidation to SO<sub>3</sub> (which subsequently forms H<sub>2</sub>SO<sub>4</sub> and condenses to form the cloud layers)

if there is an additional source of oxygen atoms (i.e., photodissociation of  $\text{CO}_2$ ) or disproportionation to form both  $\text{SO}_3$  and polysulfur,  $\text{S}_x$ , if there is no additional source of oxygen atoms. The most reducing species of sulfur that has been observed in the lower atmosphere, however, is OCS. OCS may be converted to  $\text{SO}_2$  either in the lower atmosphere, as is discussed in Sec. (3.2), or in the middle atmosphere where OCS readily undergoes photolysis:



where  $\text{S}({}^1\text{D})$  is the first electronic excited state of the S atom. The most likely fate of  $\text{S}({}^1\text{D})$  is quenching:



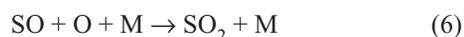
The S atom gets oxidized to SO by reacting with O and  $\text{O}_2$



Direct oxidation of OCS is also possible via



Further oxidation to  $\text{SO}_2$  can proceed via the three-body reaction



Catalytic oxidation by ClO is also possible



The rate for Reaction (7) has been measured in laboratory studies [Sander *et al.*, 2002], and Reaction (7) accounts for 10–20 % of the loss of SO at 66–80 km altitude in recent photochemical models [Pernice *et al.*, 2004; Mills and Allen, 2007]. Note that the net result is the oxidation of S to  $\text{SO}_2$ , and eventually to  $\text{H}_2\text{SO}_4$ . Plate 1 illustrates the central themes of the chemistry of Venus for the oxidation of CO and  $\text{SO}_2$ .

The ultimate fate for most  $\text{SO}_2$  in the middle atmosphere is oxidation to  $\text{H}_2\text{SO}_4$ . The spectroscopic limit on OCS above 60 km is 10 ppb while the observed  $\text{SO}_2$  mixing ratio at 40 mb (~70 km) is ~20–400 ppb, so oxidation of  $\text{SO}_2$  that has been transported upward from the lower atmosphere is the primary source for  $\text{H}_2\text{SO}_4$ . Photochemical models by Winick and Stewart [1980], Krasnopolsky and Parshev [1981abc; 1983], and Yung and DeMore [1981; 1982] show that sulfuric acid is produced mostly in a thin layer of 2 km depth centered

at 62 km. The  $\text{H}_2\text{SO}_4$  eventually forms aerosols [Winick and Stewart, 1980; Krasnopolsky and Parshev, 1981abc; 1983; Yung and DeMore, 1981; 1982; Esposito *et al.*, 1988] that are transported by the meridional circulation to the polar region where they descend into the lower atmosphere [Imamura and Hashimoto, 1998]. Thermodynamic equilibrium reactions in the lower atmosphere decompose the sulfuric acid and turn the  $\text{H}_2\text{SO}_4$  back to  $\text{SO}_2$ . This cycle of oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  followed by condensation, subsidence, evaporation, and decomposition has been termed the “fast atmospheric sulfur cycle” [von Zahn *et al.*, 1983].

In addition to oxidation to  $\text{SO}_2$  and eventually to  $\text{H}_2\text{SO}_4$ , there is another possible fate for sulfur compounds in the atmosphere of Venus: formation of polysulfur. S atoms generated by the photolysis of SO and OCS can react via



to produce  $\text{S}_2$ , or  $\text{S}_2$  may be produced via coupled S-Cl chemistry involving chlorosulfanes [Mills and Allen, 2007]. Production of  $\text{S}_3$  is possible through successive addition reactions such as



$\text{S}_3$  is the chemical analog of ozone, known as thiozone. As the number of sulfur atoms increases, the polyatomic sulfur compounds tend to have lower saturation vapor pressures. It is convenient to name all sulfur species beyond  $\text{S}_3$  “polysulfur” or  $\text{S}_x$ . The production of  $\text{S}_x$  is part of what has been termed the “slow atmospheric sulfur cycle” [von Zahn *et al.*, 1983], which is completed by decomposition reactions in the lower atmosphere (Sec. (3.2)). In the UV region  $\text{S}_x$  absorbs strongly, and it may be the principal constituent of the unidentified UV absorber in the upper atmosphere of Venus (Sec. (6)).

Whether the ultimate fate of sulfur in the middle atmosphere is  $\text{H}_2\text{SO}_4$  or  $\text{S}_x$  depends crucially on the branching for the S atom, such as Reaction (4) versus Reaction (8). For this pair of reactions, the  $\text{H}_2\text{SO}_4$  path would be preferred if

$$[\text{O}_2] > (k_8 / k_4) [\text{OCS}] \quad (10)$$

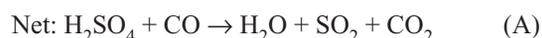
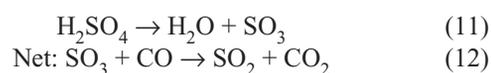
Thus when the  $\text{O}_2$  abundance exceeds this value, production of oxidized sulfur species is favored, and ultimately  $\text{H}_2\text{SO}_4$  is produced. When the  $\text{O}_2$  abundance is below this value, production of polysulfur becomes possible. Recent work on chlorosulfane chemistry [Mills and Allen, 2007] suggests the critical factor determining oxidation of sulfur versus polysulfur formation may be the oxygen to chlorine ratio,  $[\text{O}_2]/[\text{Cl}_2]$ , but the concept described here remains valid.

Since the source of  $O_2$  is photolysis of  $CO_2$  in the upper atmosphere and the source of OCS is thermodynamic equilibrium chemistry in the lower atmosphere and the surface, we can imagine that the oxygen content of the subsiding and upwelling air parcels could be quite different. This may indeed be the explanation for the patchiness and the transience of the UV markers in the cloud tops of Venus.

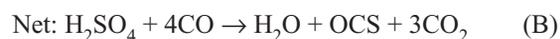
### 3.2. Sulfur Chemistry Below the Clouds

Pioneer Venus, VENERA, and ground-based observations showed that the main sulfur species in the lower atmosphere (< 60 km) is  $SO_2$  with a mixing ratio close to 150 ppm below the upper cloud [Bertaux *et al.*, 1996; Bezard *et al.*, 1993; Oyama *et al.*, 1980]. At these heights, photons with  $\lambda > 450\text{--}500$  nm are the only ones available, and the energy of sulfur atoms released by photolysis of  $S_3$  and  $S_4$  may be too low to drive endothermic reactions, so the chemistry is increasingly controlled by thermodynamic equilibrium chemistry as one goes deeper in the atmosphere. The sulfur chemistry in the lower atmosphere has been summarized in terms of three cycles, the fast and slow atmospheric cycles and the geologic cycle [von Zahn *et al.*, 1983]. The middle atmosphere portions of the fast and slow atmospheric sulfur cycles were described in Sec. (3.1). The coupling between the photochemical and thermodynamic equilibrium parts of the atmospheric cycles is shown in Plate 1.

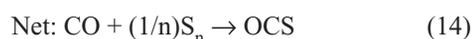
The details of the kinetic chemistry that completes the three sulfur cycles in the lower atmosphere still are largely unknown and only one kinetic model has been proposed to date. The lower atmosphere portion of the fast atmospheric cycle has been described by the net reactions [von Zahn *et al.*, 1983]



and the lower atmosphere portion of the slow atmospheric sulfur cycle has been described by the net reactions [von Zahn *et al.*, 1983]

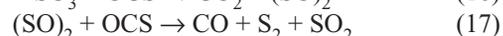
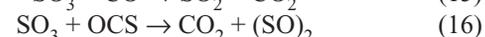
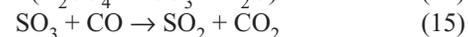


with the polysulfur branch of the slow atmospheric sulfur cycle being balanced by the net reaction [von Zahn *et al.*, 1983]



In this formulation, the net Reactions (A), (B), and (14) balance the upper atmosphere portions of the fast and slow atmospheric sulfur cycles, so there is no net production or loss of any sulfur species in the atmosphere. In a recently accepted manuscript, Krasnopolsky [2007] correctly points out that the original formulation of the slow atmospheric cycle [Prinn, 1975], which involved conversion of OCS to CO via Reaction (1), is not consistent with the observed gradient of OCS below 40 km because OCS photolyzes at wavelengths less than 285 nm and these wavelengths are absorbed by  $CO_2$ ,  $SO_2$ , and SO in or above the cloud layers. The more generalized formulation of the fast and slow atmospheric cycles [von Zahn *et al.*, 1983] quoted above, however, is consistent on a column integrated basis with the kinetic model in Krasnopolsky [2007].

Krasnopolsky and Pollack [1994] proposed a partial chemical kinetics model for the atmospheric sulfur chemistry at 20–40 km altitude that may be summarized on a column-integrated basis as:



The net process,  $2H_2SO_4 + 2OCS \rightarrow 2H_2O + 2CO_2 + S_2 + 2SO_2$ , is true only on a column-integrated basis. The relationships among the reactions at any specific altitude are more complicated, as shown in Plate 3 along with the observational data from Pollack *et al.* [1993], Marcq *et al.* [2005; 2006], and other sources. This scheme, which has been updated and extended in a recently accepted manuscript [Krasnopolsky, 2007], is the only kinetic model proposed for the lower atmosphere of Venus that is consistent with  $SO_2$  as the dominant sulfur species. The partial model did not consider sources of OCS and other processes in the  $S_x\text{--}CO\text{--}OCS$  system, although Krasnopolsky and Pollack [1994] did consider



which they said would proceed in the lowest 20 km of the atmosphere. Krasnopolsky and Pollack's scheme resulted in net destruction of OCS, which implied either the atmospheric sulfur chemistry is completed below 20 km or the atmosphere is evolving or both. Krasnopolsky and Pollack emphasized that this was only a partial solution to the problem of explaining the processes which govern profiles of OCS, CO,  $H_2SO_4$ , and  $SO_3$ , and their study did not cover some aspects of sulfur chemistry below 25 km. Krasnopolsky [2007] proposes a more complete model of the chemistry in Venus' lower atmosphere, which includes thermochemistry in the

lowest 10 km, transport downward of photochemical products from the middle atmosphere, and photodissociation of  $S_3$ . The *Krasnopolsky* [2007] model closes the atmospheric sulfur chemistry and does not result in net production or loss of any sulfur species.

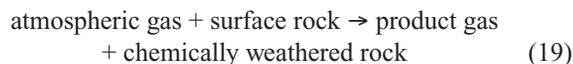
The *Krasnopolsky* and *Pollack* [1994] model is an excellent fit to the *Pollack et al.* [1993] and most other measurements at 30–45 km altitude. There is increasing disagreement between *Krasnopolsky* and *Pollack's* calculations and observations for CO as one goes toward the surface, and extrapolation of the observed CO abundances to the surface suggests CO may be in thermochemical equilibrium near the surface, based on calculations by *Fegley et al.* [1997b]. The *Krasnopolsky* [2007] model appears to agree with observations of OCS and CO over a broader altitude range than the *Krasnopolsky* and *Pollack* [1994] model. The differing  $H_2O$  profiles inferred from observations by *Ignatiev et al.* [1997] and *Meadows and Crisp* [1996] for the lowest 10 km, however, indicate further measurements are needed in the lowest scale height to properly assess the state of the chemistry at those altitudes.

The fast and slow atmospheric sulfur cycles both imply there must be a significant flux of CO from the middle atmosphere to the lower atmosphere, which is balanced by an upward flux of  $CO_2$ . The observations summarized in Section 2.5 and Plate 3, however, are more supportive of conversion between CO and OCS, at least at 30–45 km altitude. The model in *Krasnopolsky* [2007] requires a smaller flux of CO down from the middle atmosphere and proposes a mechanism for converting between CO and OCS at 30–45 km altitude, but the CO flux is still larger than in photochemical models of the middle atmosphere [*Mills et al.*, 2006; *Mills and Allen*, 2007]. The exchange of species across the cloud layers is an area that requires more study via both modelling and observations.

Although the *Krasnopolsky* and *Pollack* [1994] and *Krasnopolsky* [2007] kinetic models give good fits to extant observations, that alone should not be construed as a substitute for rigorous laboratory demonstration of the reality of Reactions (15), (16), (17), and (18). Laboratory data for many of the key reactions in this kinetic model are nonexistent or highly uncertain. Another possibility that may duplicate the net results of these reactions is heterogeneous chemistry, which could occur on aerosol particles in the lower haze layer below the lower cloud layer.

The geological cycle involves reactions between atmospheric gases and surface minerals. These chemical weathering reactions proceed slowly compared to those comprising the atmospheric cycles, so significant disequilibria may exist between the surface and the atmosphere. There have been no measurements of the surface mineralogy, although we know the abundances of Mg and heavier elements from x-ray

fluorescence spectrometers on the *VENERA* 13 and 14 and *Vega* 2 landers [*Surkov et al.*, 1984; 1986]. These elemental abundances are typical of erupted basalts. The absence of definitive data has led to speculation about what surface minerals may exist, how they may buffer the atmosphere, and how the surface-atmosphere system may have interacted over the course of Venus' evolution. The general form of the proposed reactions is [*Johnson and Fegley*, 2002]



Surface rocks that have been proposed include carbonate ( $CaCO_3$ ), wollastonite ( $CaSiO_3$ ), anhydrite ( $CaSO_4$ ), pyrite ( $FeS_2$ ), pyrrhotite ( $Fe_7S_8$ ), magnetite ( $Fe_3O_4$ ), and tremolite ( $Ca_2Mg_5Si_8O_{22}(OH)_2$ ). A number of good laboratory experiments have provided information on how rapidly chemical weathering would occur for minerals that may (or could have) existed on the surface of Venus. The experiments show that the rates for many of the posited reactions can be sensitive functions of temperature, oxygen fugacity, and/or the gaseous sulfur abundance [See Chapter 2 by *Treiman et al.*].

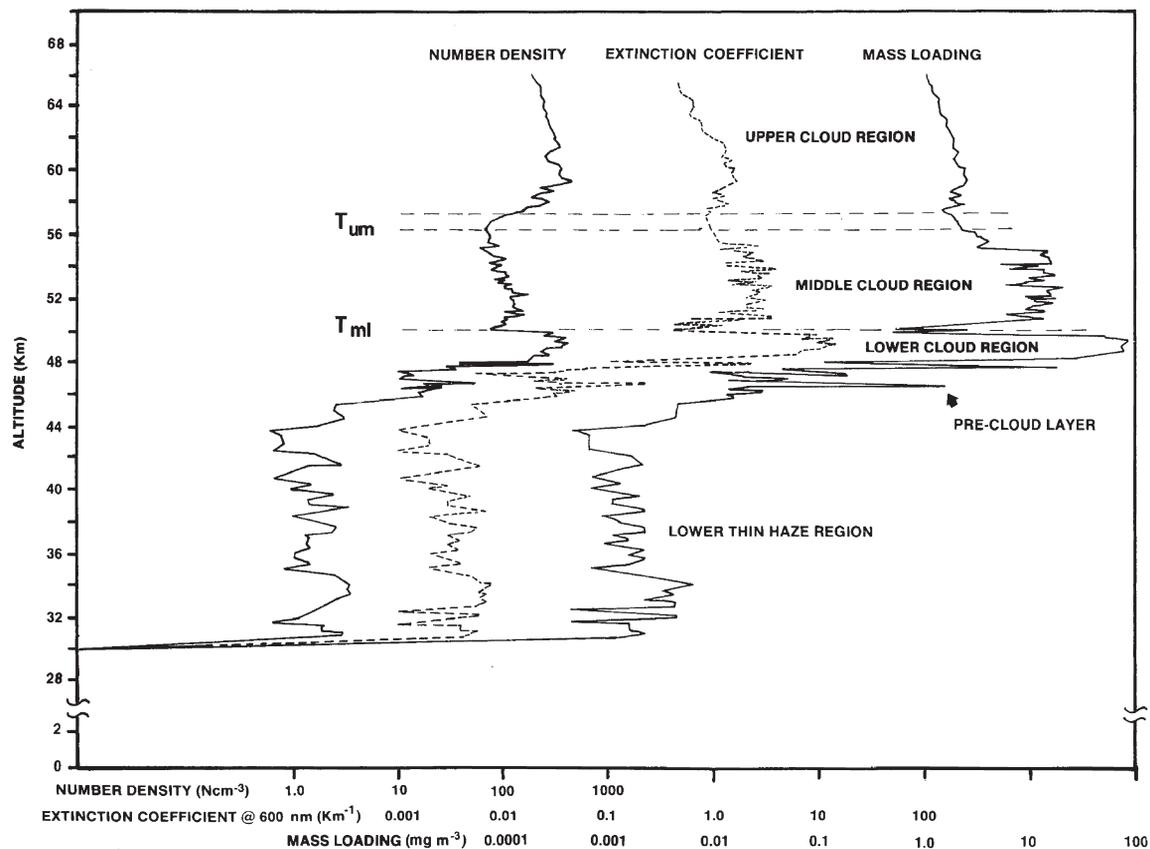
#### 4. CLOUDS

The Venus clouds and hazes have enormous vertical extent, with a lower haze down to ~30 km and an upper thick haze up to 90 km altitude; the entire system covers a vertical depth of ~60 km, with an average visibility in the Venus clouds better than several km. The main cloud deck extends from ~70 km (the level of unit optical depth in the ultraviolet) down to altitudes between 45 and 50 km.

##### 4.1. Cloud Structure, Properties, and Formation

Spacecraft *in situ* measurements allow us to divide the cloud system into upper, middle and lower clouds [see the review by *Esposito et al.*, 1983], Figure 2. Based on the Pioneer Venus and *VENERA* nephelometer results and the LCPS (Pioneer Venus Cloud Particle Size Spectrometer) measurements, it appears that the middle and upper cloud structure are planetwide features. In all cases the opacity is higher in the middle than upper cloud, typically by a factor of 2. The lower cloud is well defined and highly variable from location to location. Sharp layers are evident at the Pioneer Venus Large and Night probe sites.

The clouds within the main deck would all be thin stratoform in terrestrial classification. Instabilities are slight and latent convection potential is negligible [see *Knollenberg et al.*, 1980]. Only the middle cloud region appears to have any potential for convective overturning.



**Figure 2.** Cloud property vertical profiles.  $T_{ml}$  is the middle-lower cloud transition.  $T_{um}$  is the upper-middle cloud transition. [From Knollenberg *et al.*, 1980]

Considering the downward flux of sulfuric acid droplets, it is possible to understand why the clouds divide into three layers. Due to the photochemical formation of sulfuric acid (mostly in a thin layer of 2 km depth centered at 62 km based on models [Winick and Stewart, 1980; Krasnopolsky and Parshev, 1981abc, 1983; Yung and DeMore, 1981; 1982]), its flux increases steeply with decreasing altitude in the upper cloud layer which ends near 59 km (the measurements give 57 km). This increase correlates with the increasing  $H_2O$  mixing ratio while the concentration of sulfuric acid is relatively constant.

The flux of liquid sulfuric acid is constant in the middle cloud layer (57–50 km according to the measurements).

In the models by Krasnopolsky and Pollack [1994], the lower cloud layer forms at 48–47 km, where the predicted flux of liquid sulfuric acid exceeds that in the middle cloud layer by a factor of 4–7. The  $H_2O$  mixing ratio is rather constant, and thus the water fraction continues to decrease by a factor of 3 until the lower cloud boundary is reached. This corresponds to the acid concentration increasing to 97–98% at the lower cloud boundary. A strong gradient of gaseous sulfuric acid drives an upward flux which condenses and forms a strong downward flux of liquid sulfuric acid with the

sum of both fluxes being constant in the lower and middle cloud layers. According to Krasnopolsky and Pollack [1994], this is the mechanism of the formation of the lower cloud layer. Thus, the upper cloud is created by photochemical production, the middle cloud by droplet growth and sedimentation, and the lower cloud by condensation enhancing the downward flux.

Krasnopolsky and Pollack [1994] developed a method to calculate the lower cloud boundary, with results between 48.4 km and 46.6 km. This is in good agreement with the PV radio occultation observations [Cimino, 1982], which show the boundary varying from 47–48 km at the low and middle latitudes and 47–43 km at high and subpolar latitudes.

The location of the lower boundary varies due to variations of the  $H_2SO_4$  vapor mixing ratio, the water vapor mixing ratio below the clouds, and temperature and pressure. Krasnopolsky and Pollack [1994] found the boundary variations are produced mostly by variations of the sulfuric acid abundance and temperature. Variations of density in the lower cloud layer reflect variations of gaseous sulfuric acid, because water contributes only slightly to the sulfuric acid aerosol in the lower cloud layer.

#### 4.2. The Mode 3 Particle Controversy

The Pioneer Venus LCPS measurement of larger, so called “Mode 3” particles has provided a controversy that is still unresolved; see *Esposito et al.* [1983]. The starting point for the Mode 3 controversy comes from direct evidence for asymmetric (possible crystalline) particles provided by *Knollenberg and Hunten* [1980]. *Knollenberg et al.* [1980] further state that only such crystals of high aspect ratio could satisfy the Pioneer Venus LCPS, LSFR, and LN results simultaneously. However, since the largest amount of mass (~80% according to *Knollenberg and Hunten* [1980]) is within the Mode 3 particles, it is extremely important to verify their existence and determine their composition.

The LCPS undoubtedly detected large particles, but the evidence for solid particles is indirect. There were internal inconsistencies in the LCPS measurements as well as inconsistencies between the LCPS measurements and the measurements made by other instruments. Some of these inconsistencies were:

1. Calculations employing LCPS size distributions do not give the backscatter observed by the PV nephelometer in the lower clouds if reasonable refractive indices are used.
2. The LCPS size distributions do not yield the optical depths derived by the LSFR, assuming spherical particles.
3. Overlapping size ranges of the LCPS give conflicting measurements in the lower clouds.

In addition, independent VENERA results show some oddities at the same altitudes:

1. VENERA nephelometer phase function measurements are inconsistent with spherical particles having reasonable refractive indices in the lower cloud.
2. X-ray fluorescence measurements [*Surkov*, 1979] show about ten times as much chlorine as sulfur in the Venus clouds.

The various inconsistencies can be explained by the simple hypotheses that Mode 3 is composed of solid, nonspherical particles. However this explanation requires an abundant gas-phase chemical in the clouds as the source for these particles. No such gas has yet been discovered.

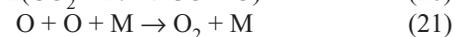
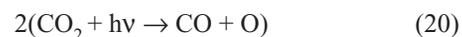
*Toon et al.* [1982] reexamined the evidence that solid particles form a distinctive size mode. They find that Mode 3 is defined by a discontinuity located between two size ranges of the LCPS. Although this could be real, it could also be the result of a small calibration shift of the PV instrument. A shift in the calibration removes the discontinuity, along with the internal inconsistency of the LCPS. The revised size spectrum is consistent with the VENERA and Pioneer Venus optical data in the lower clouds; all the modes can be composed of sulfuric acid droplets without any solid par-

ticles. The only unexplained data are those showing large amounts of chlorine compared to sulfur in the clouds. We note, though, that the more recent Soviet measurements from VENERAs 13 and 14 show a large sulfur to chlorine ratio, the opposite of *Surkov's* [1981] findings. The VEGA landers detected no large particles.

From the data in hand, it seems impossible to disprove the existence of Mode 3. Two self-consistent, alternative interpretations of the data exist. Accepting the spacecraft observation at face value, we are led to the existence of a mode of large solid non-spherical particles whose composition is unknown and whose source vapor has escaped detection. On the other hand, we may conclude that the large particle mode is merely the (mis-measured) tail end of the Mode 2 sulfuric acid droplets. This allows a simple understanding of the source of all the cloud particles, but at the cost of disbelieving some of the measurements.

#### 5. CHLORINE CHEMISTRY

The most important consequence of photochemistry in the Venus atmosphere is the breaking of the strong O-CO bond, yielding O<sub>2</sub>,



The central problem of Venus photochemistry, thus, is the very low observational limit on the abundance of O<sub>2</sub>. The observed large production rate of O<sub>2</sub> [*Connes et al.*, 1979; *Crisp et al.*, 1996] combined with the low upper limit on its abundance implies either a large reservoir in which oxygen is sequestered or fast oxidation of CO and/or SO<sub>2</sub>, or all three. The abundance of O<sub>2</sub> is determined by the sulfur oxidation cycle, as described in Sec. (3.1), and the CO<sub>2</sub> cycle, which is the dominant chemical cycle above the cloud layers (>~ 70 km altitude). Hydrogen, chlorine, and sulfur chemistries are all linked to the CO<sub>2</sub> cycle, but chlorine chemistry is believed to provide the critical pathway for catalyzing oxidation of CO to CO<sub>2</sub> [*Krasnopolsky and Parshev*, 1981abc; 1983; *Yung and DeMore*, 1981; 1982; *Pernice et al.*, 2004].

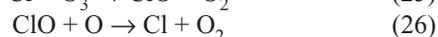
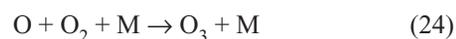
Observations in 1966 [*Connes et al.*, 1967] detected a substantial (0.4–0.6 ppm at 67–70 km altitude [*Connes et al.*, 1967; *Young*, 1972]) abundance of HCl. HCl should be the dominant source of hydrogen and chlorine radicals at ~ 75–95 km because (1) the water vapor abundance should be suppressed by condensation onto the concentrated sulfuric acid particles in the upper haze layer [*Mills*, 1999a] and (2) photodissociation of H<sub>2</sub>O is strongly attenuated below 100

km by CO<sub>2</sub> photoabsorption while photodissociation of HCl is still significant at 75 km.

Detection of HCl led to proposals that CO oxidation occurs via Reactions (22) and (23) [Prinn, 1971; Sze and McElroy, 1975].

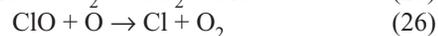
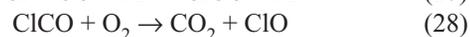
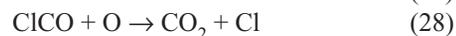


Subsequent laboratory studies, however, showed these reactions proceed too slowly to be significant. The next advances in understanding chlorine chemistry in the Venus atmosphere came in the early 1980s after VENERA 11 and 12 and near the beginning of the Pioneer Venus mission. Three modeling studies of increasing complexity and accuracy were published. *Winick and Stewart* [1980] introduced the first model with both sulfur and chlorine chemistry, including the now classic chlorine cycle for converting odd oxygen to molecular oxygen, Reactions (25) and (26).



This cycle was so efficient it completely balanced the new sulfur cycles involving Reaction (4) that *Winick and Stewart* [1980] introduced to break the O-O bond. Consequently, the predicted O<sub>2</sub> column abundance was a factor of 50 larger than the then extant upper limit (and a factor of 150 larger than the current upper limit).

The next two modeling studies independently developed the chemistry of the chloroformyl radical (CICO) and identified it as a potentially significant intermediary in the production of CO<sub>2</sub>. These schemes involving CICO are the only ones proposed to date that operate efficiently in the 75–90 km altitude region where CO<sub>2</sub> photodissociation is largest. The two schemes introduced by *Krasnopolsky and Parshev* [1981abc; 1983] for oxidation of CO via CICO are

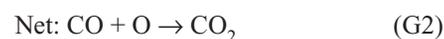
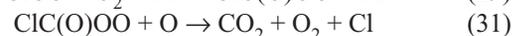
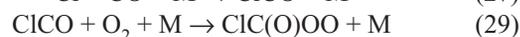
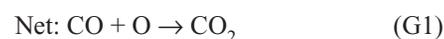
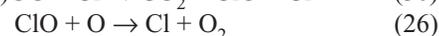
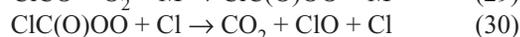


Neither of these breaks the O-O bond in O<sub>2</sub>. There are two major problems with the Krasnopolsky and Parshev model. First, the equilibrium constant for CICO in the compilation from which they drew their laboratory data [Kondratiev, 1971] was incorrect due to a typographical error and implied CICO was two orders of magnitude more stable than laboratory studies had found. Second, independent laboratory studies [Yung and DeMore, 1982] found the mechanism postulated for Reaction (28) was incorrect. Production of CO<sub>2</sub> instead proceeds via the peroxychloroformyl radical (CIC(O)OO or ClCO<sub>3</sub>), which is produced by Reaction (29).



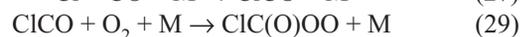
However, the Krasnopolsky and Parshev model calculated a much smaller O<sub>2</sub> abundance than any other model developed in the 1980's.

*Yung and DeMore* [1981; 1982] independently introduced three schemes for oxidation of CO via CICO. Two are



Neither of these schemes breaks the O-O bond in O<sub>2</sub> but *Yung and DeMore's* [1981; 1982] third scheme, which is discussed in Sec. (7.1), does. The primary failing of the *Yung and DeMore* [1981; 1982] models was that the calculated column abundance of ground-state O<sub>2</sub> was larger than the upper limit derived from observations made in 1983 [Trauger and Lunine, 1983].

Reaction (29) is the key step in what are believed to be the dominant gas-phase pathways for production of CO<sub>2</sub> in the Venus atmosphere, Figure 3. Production of CO<sub>2</sub> via pathways that include Reaction (29) accounted for 80% of the column total CO<sub>2</sub> production in the *Yung and DeMore* [1982] model C, and the four pathways in *Pernice et al.* [2004] that are most important for oxidation of CO are Schemes (E), (G1), (G2), and (G3).

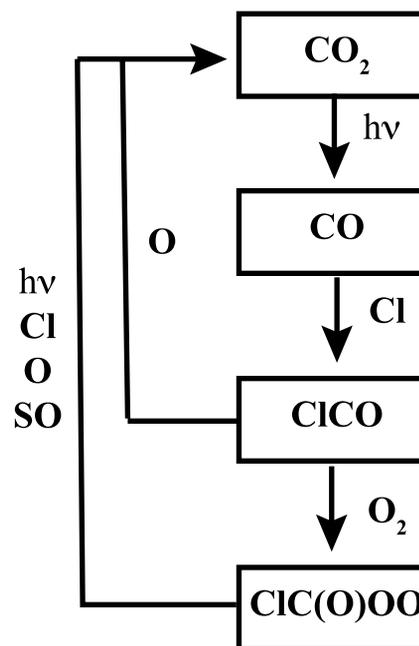




Scheme (G1) accounts for 54% of the column total  $\text{CO}_2$  production in the *Pernice et al.* [2004] model while Schemes (E), (G2), and (G3) account for 19, 10, and 12%, respectively, of the column total  $\text{CO}_2$  production in that model. The contributions of each of these pathways to oxidation of CO in the  $+2\sigma$  model in Table 5 are comparable.

Recent calculations [Mills, 1998; Pernice et al., 2004] have shown that a model using these gas-phase pathways can be brought into better agreement with the extant upper limit on  $\text{O}_2$  [Trauger and Lunine, 1983; Mills, 1999b; Krasnopolsky, 2006b] by enhancing the stability of CICO within its experimental uncertainty. However, none of the models that oxidize CO only via gas-phase processes agrees with the published  $2\sigma$  upper limits on the column abundance of ground-state  $\text{O}_2$  [Trauger and Lunine, 1983; Krasnopolsky, 2006b]. The smallest observational upper limit is equivalent to a column abundance of  $8 \times 10^{17} \text{ cm}^{-2}$  [Krasnopolsky, 2006b], but there is disagreement over the interpretation of this observation [Mills, 1999b; Krasnopolsky, 2006b]. In addition, the improvement in the agreement with the  $\text{O}_2$  observational upper limit achieved in later models [Mills, 1998; Pernice et al., 2004] may create a disagreement with the CO vertical profile, but the observational constraints for CO from ground-based studies are not definitive, particularly on the day side and in the upper cloud [Mills and Allen, 2007].

There are three critical steps in the primary gas-phase pathway for production of  $\text{CO}_2$ , Figure 3: formation of CICO; association of CICO with  $\text{O}_2$  to form ClC(O)OO before CICO thermally decomposes; and formation of  $\text{CO}_2$  from ClC(O)OO. All three critical steps now have been observed in laboratory studies, so this reaction mechanism may be considered validated. The formation of CICO and its thermal stability were studied most recently by *Nicovich et al.* [1990]. The assessed uncertainties in their results for heat of formation and reaction enthalpy are  $\sim 1.5 \text{ kcal/mol}$  and in the reaction entropy is  $\sim 5 \text{ cal/mol/K}$  [Sander et al., 2002]. Formation of ClC(O)OO via Reaction (29) was demonstrated in cryogenic



**Figure 3.** Schematic showing primary pathways for production of  $\text{CO}_2$  via chlorine chemistry. The reaction  $\text{CICO} + \text{O} \rightarrow \text{CO}_2 + \text{Cl}$  accounts for 15 and 20% of the column total  $\text{CO}_2$  production in the  $+0.5\sigma$  and  $+2.0\sigma$  models from Table 5, respectively.

matrix experiments [Pernice et al., 2004] and a gas phase rate for production in laboratory studies has been reported [Yung and DeMore, 1982]. Other experiments reported in *Pernice et al.* [2004] demonstrated the formation of  $\text{CO}_2$  from photodissociation of ClC(O)OO, derived the UV absorption spectrum for ClC(O)OO, and determined that ClC(O)OO is thermally stable at temperatures below 350 C.

Substantial uncertainties remain, however, in the rates at which each of the three critical steps occur in Venus' atmosphere. The experimental uncertainty in the equilibrium constant for CICO can be expressed in terms of Equation (33) for 200–300 K [Sander et al., 2002]

$$f(T) = f(298 \text{ K}) \exp[\Delta B((1/T) - (1/298))], \quad (33)$$

where  $f$  = uncertainty,  $T$  = temperature,  $\Delta B$  = uncertainty in the equilibrium constant's exponential factor which

**Table 5.** Sensitivity of modeled  $\text{O}_2$  column abundance to thermal stability of CICO in baseline chlorine chemistry model [Pernice et al., 2004].

CICO stability	$+2\sigma^a$	$+1\sigma$	$+0.5\sigma$	Nominal	$-0.5\sigma$	$-1\sigma$	$-2\sigma^b$
$\text{O}_2$ column abundance ( $10^{18} \text{ cm}^{-2}$ )	2.0	2.4	3.1	8.6	27	39	49

<sup>a</sup> Increased the thermal stability of CICO by twice the assessed uncertainty in its equilibrium constant [Sander et al., 2002].

<sup>b</sup> Decreased the thermal stability of CICO by twice the assessed uncertainty in its equilibrium constant [Sander et al., 2002].

is 500 K for ClCO, and  $f(298) = 5$  for ClCO. Although small by experimental standards, the uncertainty in the equilibrium constant for ClCO translates into a large uncertainty in the predicted O<sub>2</sub> profile [Mills, 1998] and in the calculated O<sub>2</sub> column abundance, as illustrated in Table 5. No experimental uncertainty has been reported for Reaction (29) and only one laboratory study of this reaction rate is published [Yung and DeMore, 1982]. No experimental measurements exist for the rates at which ClC(O)OO reacts with any of the important radicals in the Venus atmosphere (e.g., O, SO, Cl), although production of CO<sub>2</sub> from photodissociation of ClC(O)OO has been demonstrated [Pernice et al., 2004].

None of the chlorine radicals has yet been observed in Venus' atmosphere. Their detection would provide a major confirmation of this proposed model.

## 6. UNIDENTIFIED UV AND BLUE ABSORPTION

Currently, the only positively identified species in the visible atmosphere that absorb in the near UV are SO<sub>2</sub> and SO. These gases can account for the absorption observed at wavelengths short of 320 nm at all altitudes [Esposito, 1980; Pollack et al., 1980] and for the absorption observed at 320–390 nm below 55 km [Ekonomov et al., 1983]. However, they cannot account for the absorption observed in the upper cloud at wavelengths longward of 320 nm, nor can they account for the absorption observed at 400–500 nm [Esposito, 1980; Pollack et al., 1980; Ekonomov et al., 1983]. In addition, these other absorbers must explain the phase angle dependence of the UV dark markings [Barker et al., 1975] as well as their short lifetime above the clouds (from hours to days, see Esposito et al. [1983]). They must also be consistent with the visible-wavelength solar flux observations of Tomasko et al. [1980] which show absorption at 58–62 km, and little absorption below. Near UV solar flux absorption results from VENERA 14 [Ekonomov et al., 1983; 1984] provide an additional constraint. Esposito and Travis [1982] noted the correlation between dark markings seen longward of 320 nm and SO<sub>2</sub> enhancements seen at 207 nm. This means that in addition to the absorption spectrum, a good candidate must also match constraints on its vertical distribution, lifetime, and correlation with SO<sub>2</sub> enhancement. This last correlation could be either chemical or dynamical because the SO<sub>2</sub> observable in the middle UV is likely the result of local upwelling [Esposito and Travis, 1982]. We briefly review the suggested candidates below.

**S<sub>8</sub>.** S<sub>8</sub> was proposed by Hapke and Nelson [1975] and Young [1977, 1983] as the second absorber since it absorbs strongly in the UV. However, Pollack et al. [1980] showed that the spectral characteristics of S<sub>8</sub> were inconsistent with

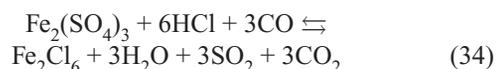
those of the second absorber. Another shortcoming of S<sub>8</sub> as the second absorber is its vertical profile. S<sub>8</sub> is not expected to disappear rapidly below the upper cloud layer since it precipitates as a solid, and the idea of these particles hiding inside sulfuric acid aerosols has been discounted by Young [1983]. Thus, the vertical profile of S<sub>8</sub> does not match that of the second absorber. Furthermore, the chemical lifetime of S<sub>8</sub> above the clouds is much longer than the timescale of the dark markings, thus it is difficult to explain the rapid disappearance (lifetime <3 hours) of small scale dark markings [e.g., Rossow et al., 1980].

**S<sub>3</sub> and S<sub>4</sub>.** Toon et al. [1982] suggested metastable sulfur allotropes, S<sub>3</sub> and S<sub>4</sub>, as the most likely candidate for the second absorber. The absorption cross sections of S<sub>3</sub> and S<sub>4</sub> peak around 400 and 520 nm, respectively. The combination of these two sulfur gases with SO<sub>2</sub> provides a very close match to the albedo of Venus. The peak in the absorption cross sections of S<sub>3</sub> around 400 nm lines up with a kink in the albedo spectrum of Venus. S<sub>3</sub> and S<sub>4</sub> are metastable, and once produced they quickly relax to S<sub>8</sub> which exists as particulates. In this model, the S<sub>8</sub> would therefore contribute less. It is not clear if this contradicts Young's assertion (above). S<sub>8</sub> particles could then become incorporated into the sulfuric acid aerosols and fall out of the cloud region. This scenario thus explains the short lifetime of the dark features and the absence of the second absorber below the upper clouds. Furthermore, these sulfur allotropes can account for the high real refractive index of the upper cloud material, and the bimodal size distribution observed in the Venus clouds. When there is little oxygen in the atmosphere, sulfur allotropes can be produced from SO<sub>2</sub> photolysis instead of sulfuric acid [Prinn, 1975, 1985], so S<sub>3</sub> and S<sub>4</sub> may be produced in areas where sulfur vapor is enriched. However, there has been no positive detection of S<sub>3</sub> or S<sub>4</sub> to date. Further, these allotropes are rapidly photo-dissociated, giving lifetimes close to 1 second in the upper cloud. One further problem with the above scenario is that sulfur particles would still absorb UV photons below the upper clouds.

**Cl<sub>2</sub>.** Pollack et al. [1980] proposed Cl<sub>2</sub> as a candidate for the second absorber. Pollack et al. showed that about 1 ppm of Cl<sub>2</sub> in the upper cloud could produce the brightness contrast seen in the UV images of the clouds. Cl<sub>2</sub> may exist in the atmosphere of Venus since it is produced from photodissociation of HCl which was detected in the atmosphere of Venus by Connes et al. [1967]. Some of the difficulties of Cl<sub>2</sub> being the second absorber include the relative scarcity of HCl in the atmosphere. The photochemical calculations of Winick and Stewart [1980], Krasnopolsky and Parshev [1981abc; 1983], and Yung and DeMore [1981; 1982] showed that the amount of Cl<sub>2</sub> produced from HCl photolysis is two orders of magnitude smaller than 1 ppm. Furthermore, the

vertical profile shows no maximum around 60 km, or rapid decline below 58 km. Finally, there is no obvious chemical or dynamical connection between  $\text{Cl}_2$  and  $\text{SO}_2$ .

**FeCl<sub>3</sub>.** Ferric Chloride is a possible candidate to explain absorption in the cloud layer. *Krasnopolsky* [1985, 1986] showed that many properties of the clouds can be explained if condensation of  $\text{Fe}_2\text{Cl}_6$  vapor occurs at 47.5 km at the PV sounder probe site. This means that this species' mixing ratio is equal to 15 ppbv below 47.5 km. The calculated profile of the  $\text{FeCl}_3$  condensate coincides with that of the mode 1 particles in the lower and middle cloud layer. The mode 1  $\text{FeCl}_3$  particles can then be transported by eddy diffusion to the upper cloud layer where they serve as condensation centers for the mode 2  $\text{H}_2\text{SO}_4$  particles. These particles are liquid below 62–63 km, and the ratio of the  $\text{FeCl}_3$  flux to the  $\text{H}_2\text{SO}_4$  production rate corresponds to a solution with concentration of  $\text{FeCl}_3$  close to 1%. It is this solution which can explain the 320–500 nm absorption [*Zasova et al.*, 1981]. The reaction between  $\text{FeCl}_3$  and concentrated  $\text{H}_2\text{SO}_4$  is rather slow at temperatures 250–280 K at 62–58 km, and the lifetime of the solution is close to the precipitation time of one month. Colorless ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , replaces  $\text{FeCl}_3$  near 58 km. In thermochemical equilibrium:



it is favorable to form  $\text{Fe}_2\text{Cl}_6$  vapor throughout the atmosphere.  $\text{FeCl}_3$  in aerosol particles was observed by X-ray fluorescent spectroscopy from the VENERA 14 and VEGA landers [*Petryanov et al.*, 1981; *Andreichikov et al.*, 1987; *Krasnopolsky*, 1989]. The transition from  $\text{FeCl}_3$  to colorless ferric sulfate predicted to occur at 58 km is close to the lower boundary of absorption observed by *Ekonomov et al.* [1983, 1984] on VENERA 14.

**SCl<sub>2</sub>.** *Krasnopolsky* [1986] found a mixture of sulfur aerosol and  $\text{SCl}_2$  fits well the absorption, but the required mixing ratio for  $\text{SCl}_2$  of  $10^{-7}$  exceeds his estimate of its mixing ratio by at least an order of magnitude. The  $\text{SCl}_2$  mixing ratio in the models whose results are shown in Table 5 and in *Pernice et al.* [2004] is less than  $10^{-9}$  with the maximum in the lowest layer at 58 km altitude.

**Croconic acid.** *Hartley et al.* [1989] proposed croconic acid ( $\text{C}_5\text{O}_5\text{H}_2$ ) as a candidate for the second absorber based on their measurement of its absorption spectrum. They carried out radiative transfer calculations to show that sulfuric acid aerosols mixed with 2.5% of croconic acid can produce the observed UV contrast in the clouds of Venus. According to *Hartley et al.* [1989], croconic acid can be produced by reactions involving CO and  $\text{HO}_x$ , for example, in the equilibrium



Its production is proportional to  $[\text{CO}]^6$  and should be maximum near 40 km, because this acid decomposes at 40 km ( $T = 150^\circ\text{C}$ ). All these facts reduce the possibility of  $\text{C}_5\text{O}_5\text{H}_2$ . *Widemann et al.* [1993] reported a negative detection of croconic acid in the spectra of Venus' atmosphere taken with the VEGA probe.

**Ammonium pyrosulfite.** *Titov* [1983] studied the formation of aerosol in a mixture of  $\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , and found that ammonium pyrosulfite,  $(\text{NH}_4)_2\text{S}_2\text{O}_5$ , resulted from the mixture. He studied the absorption spectrum of  $(\text{NH}_4)_2\text{S}_2\text{O}_5$  and found that the mixture of  $\text{NH}_3$  with  $\text{H}_2\text{SO}_4$  has spectral characteristics similar to that of the second absorber. *Krasnopolsky* [1985] points out that formation of ammonium pyrosulfate is enhanced at low temperatures. This would predict an anti-correlation between the albedo at 365 nm and the radiance at 11.5  $\mu\text{m}$  (this latter wavelength is sensing the upper cloud temperature), which is not seen in PV observations.

**Nitrosylsulfuric acid.**  $\text{NOHSO}_4$  [*Watson et al.*, 1979; *Sill*, 1983]. Unfortunately, it only has weak blue absorption and requires the presence of NO and  $\text{NO}_2$  with abundances that seem incompatible with the upper limit of 6 ppb for  $\text{NO}_2$  and with the expected production of NO by lightning if it really occurs on Venus. These negative comments are still true, although *Krasnopolsky* [2006a] has observed 5.5 ppb of NO below 60 km.

**S<sub>2</sub>O.** *Hapke and Graham* [1985, 1989] proposed that disulfur monoxide ( $\text{S}_2\text{O}$ ) and polysulfur oxides (PSO) may be responsible for the UV markings in the clouds of Venus. They measured the relative reflectance of  $\text{S}_2\text{O}$  frost at 77K, and found that it has a low reflectivity in the wavelength region from 200 to 500 nm. *Na and Esposito* [1997] estimated the chemical lifetime and vertical distribution of  $\text{S}_2\text{O}$ , both of which match the second absorber, although calculations by *Mills* [1998] found  $\text{S}_2\text{O}$  abundances significantly smaller than those calculated by *Na and Esposito* [1997] for reasons that have not been resolved. Its obvious chemical connection with  $\text{SO}_2$  could explain the correlations of the dark markings with  $\text{SO}_2$  enhancements. Unfortunately, we do not have a good spectrum measured for the gas phase. In addition, recent *ab-initio* calculations [*Groves and Lewars*, 2000] suggest  $(\text{SO})_2$ , the precursor to  $\text{S}_2\text{O}$ , may not be as stable as has been assumed but there are no experimental data.

Of the candidates discussed above, elemental sulfur and ferric chloride solution in sulfuric acid are the most promising candidate species for explaining the observed absorption at 320–500 nm, perhaps even in combination.  $\text{S}_2\text{O}$  may also be important but there are significant uncertainties in both

its spectrum and its chemistry. Further laboratory studies are required to address existing uncertainties in the spectral characteristics of the candidate species and their chemistry. Venus Express images and spectra may allow progress on this topic. For example, a correlation of dark  $S_x$  markings in VIRTIS-M data at multiple wavelengths where  $S_x$  is a strong absorber would be good evidence for the presence of  $S_x$  [Carlson, 2007]. However, in situ measurements within the clouds provide the only prospect for a secure identification. This must await a future Venus mission.

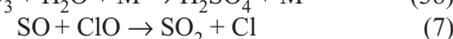
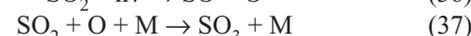
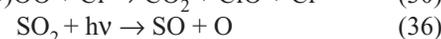
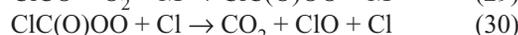
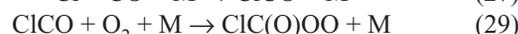
## 7. EMERGING DEVELOPMENTS: COUPLING AMONG CYCLES AND NITRIC OXIDE

### 7.1. Coupling Among Chemical Cycles

The three chemical cycles couple at a number of key points. First, as discussed in Sec. (2.6), the middle and lower atmosphere portions of the two sulfur cycles are believed to balance each other, on the assumption that the atmosphere is near a long-term equilibrium point. However, little modeling has been done across the boundary between photochemistry and thermochemistry and there appear to be inconsistencies between the best fit solutions derived for each altitude region. *Esposito et al.* [1997] provide an excellent discussion of these issues, so only a summary is provided here. Model 1 from *Krasnopolsky and Pollack* [1994] assumed a lower production rate for  $H_2SO_4$  ( $2.2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ ), placed the lower cloud boundary at 48.4 km (agreeing with *in-situ* data), and predicts the  $H_2O$  mixing ratio is 30 ppm at 30 km (agreeing with *Pollack et al.* [1993]). Model 1 can be roughly correlated with *Yung and DeMore's* [1982] Model C, which has good kinetic data for the middle atmosphere. Model 2 from *Krasnopolsky and Pollack* [1994] assumed a higher production rate for  $H_2SO_4$  ( $6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ ), placed the lower cloud boundary at 46.5 km (agreeing with radio occultations), and predicts the  $H_2O$  mixing ratio is 90 ppm at 30 km (close to *Moroz et al.* [1983]). Model 2 can be roughly correlated with *Krasnopolsky and Parshev's* [1981abc; 1983] photochemical model. A newer analysis of the *Venera* optical spectra using a high temperature spectroscopic database [*Ignatiev et al.*, 1997] found an abundance for  $H_2O$  at 30 km that agrees well with the interpretation of ground-based observations [*Pollack et al.*, 1993], so Model 1 is now strongly favored on that basis. In addition, *Yung and DeMore's* [1982] Model C has much firmer photochemical data. The predicted  $O_2$  column abundance from Model C, however, exceeds the spectroscopic upper limit by an order of magnitude, although more recent models based on the *Yung and DeMore* [1981; 1982] Model C chemistry [*Pernice et al.*, 2004] show better agreement. *Krasnopolsky and Parshev's* [1981abc; 1983]

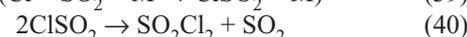
model overpredicts the  $O_2$  column abundance by only a factor of two but key kinetic data underlying the calculations were not correct (Sec. (5)). Modeling and data over the depth of the cloud layers are needed to resolve these apparent conflicts.

The  $CO_2$  and sulfur oxidation cycles are also linked near the cloud tops in a manner that can efficiently break the O-O bond in  $O_2$  [*Yung and DeMore*, 1981; 1982]. The essence of the chemical scheme may be summarized as



where  $ClC(O)OO$  is the peroxychloroformyl radical and  $M$  is a third body (ambient atmosphere). Note that this scheme oxidizes  $SO_2$  to  $H_2SO_4$  while oxidizing  $CO$  to  $CO_2$ . The relative importance of Scheme (H), when compared to Schemes (G1), (G2), and (G3), determines the efficiency with which the O-O bond in  $O_2$  is broken. Scheme (H) has a solid basis in laboratory kinetic data (Sec. (5)) but likely requires vertical transport of  $SO$  because photodissociation of  $CO_2$  occurs predominantly above 75 km altitude while photodissociation of  $SO_2$  occurs predominately below 70 km altitude. Vertical transport of significant amounts of  $O_2$  would likely require violating the observational upper limit on its abundance, and the lifetime of  $ClO$  should be short.

$Cl-SO_2$  interaction can lead to formation of sulfuryl chloride,  $SO_2Cl_2$ , [*DeMore et al.*, 1985] via



The rate for Reaction (39) has been determined in laboratory studies [*Stratton et al.*, 1979; *Eibling and Kaufman*, 1983], although none of the work was conducted in  $CO_2$ . The rate for Reaction (40) has not been determined but quantitative evidence of the production of  $SO_2Cl_2$  from photolysis of a mixture of  $Cl_2$  and  $SO_2$  has been found in laboratory experiments [*DeMore et al.*, 1985].

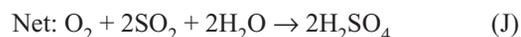
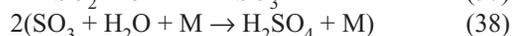
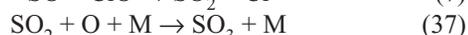
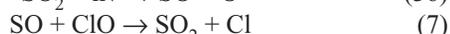
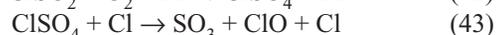
The inclusion of Reaction (39) but not Reaction (40) in the models whose results are presented in Table 5 increases the  $SO_2$  scale height near 70 km altitude from  $\sim 2.5$  km [*Yung*

and DeMore, 1981; 1982] to  $\sim 3.0$ – $3.5$  km, both of which are within the 2–4 km observational constraint [Na *et al.*, 1994]. This buffering of  $\text{SO}_2$  also contributes to decreasing the  $\text{H}_2\text{SO}_4$  production rate from  $1.4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  [Yung and DeMore, 1982] to  $\sim 5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ , which is closer to an early observational estimate of the  $\text{H}_2\text{SO}_4$  production rate,  $\sim 2 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$  [Winick and Stewart, 1980]. All of the production rates for  $\text{H}_2\text{SO}_4$  from these photochemical models are smaller than those required to match either model from Krasnopolsky and Pollack [1994]. In addition, Krasnopolsky [2006a] found that inclusion of  $\text{NO}_x$  in a photochemical model opened an additional important pathway for oxidizing SO



which may further reduce the modeled  $\text{H}_2\text{SO}_4$  production rate. If the  $\text{H}_2\text{SO}_4$  production rate is as large as has been modeled by Krasnopolsky and Pollack [1994], then a critical process may be missing from current photochemical models.

One way the rate of formation of sulfuric acid might be enhanced is via Cl- $\text{SO}_2$  interactions

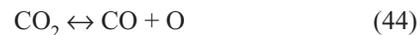


DeMore *et al.* [1985] proposed these processes could be quite important in Venus' atmosphere and demonstrated quantitative production of  $\text{H}_2\text{SO}_4$  from irradiated mixtures of  $\text{Cl}_2$ ,  $\text{SO}_2$ , and  $\text{O}_2$  in which the yield of  $\text{H}_2\text{SO}_4$  (versus  $\text{SO}_2\text{Cl}_2$ ) increased as the partial pressure of  $\text{O}_2$  increased, but they have not been developed further. More specific information from laboratory experiments on the reaction mechanism and the rates of the reactions leading to production of  $\text{H}_2\text{SO}_4$  is needed. The interaction of chlorine and sulfur chemistry in the Venus cloud layers merits further study as it provides key links among the primary chemical cycles and may provide a mechanism to sequester oxygen for transport to the lower atmosphere.

## 7.2. Nitric Oxide (NO)

Lightning is equivalent to thermodynamic equilibrium chemistry at high temperatures, initially in excess of 30,000

K in the fireball, but as temperature decreases rapidly due to adiabatic expansion, the constituents are quenched at about 2000 K. The net result may be summarized by the chemical scheme [Yung and McElroy, 1979],



This scheme is analogous to that operating in the present terrestrial atmosphere [Price *et al.*, 1997], where NO is made via the chemical scheme,



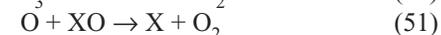
On Venus, as it was on prebiotic Earth,  $\text{CO}_2$  replaces  $\text{O}_2$  as the oxidant for  $\text{N}_2$ . The NO is eventually removed by reactions above the cloud tops,



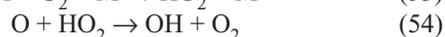
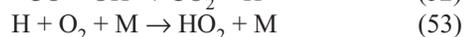
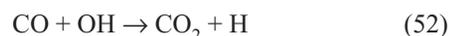
## 8. COMPARISONS TO OTHER PLANETS

### 8.1. Comparisons Among Venus, the Earth, and Mars

Catalytic chemistry plays fundamental roles in the atmospheres of all three planets [see, *e.g.*, Yung and DeMore, 1999]. This means trace abundances of highly reactive radicals govern the primary chemical cycles on each planet. On Venus, a small amount of Cl has a major impact on the production of  $\text{CO}_2$  from CO and  $\text{O}_2$ . On the Earth, hydrogen, nitrogen, and halogen radicals play an analogous role. The most prominent example is the regulation of the stratospheric ozone layer. A large number of the catalytic cycles are of the form



where X = H, OH, NO, Cl and Br. The net result of these catalytic cycles is the destruction of  $\text{O}_3$ . On Mars the key catalytic cycle that recombines CO and O to form  $\text{CO}_2$  involves hydrogen radicals [McElroy and Donahue, 1972].



A similar scheme by *Parkinson and Hunten* [1972] is also important.

The greatest difference between Venus and Earth concerns the amount of water on these two planets [see, *e.g.*, *Yung and DeMore*, 1999]. The mixing ratio of water vapor in the lower atmosphere of Venus is variable, with a maximum value of  $1.5 \times 10^{-4}$ . This is equivalent to a layer of 2–10 cm of water, uniformly spread over the surface of the planet. For comparison, Earth contains an average layer of 2.7 km of water, residing mostly in the oceans. The lack of an ocean on Venus has at least three dramatic consequences for the atmosphere. First, most of the planet's  $\text{CO}_2$  remains in the atmosphere, in contrast to Earth, where most of the 50 bars of  $\text{CO}_2$  are sequestered as carbonate rock in the sediments. Second, the atmosphere of Venus contains large quantities of  $\text{SO}_2$ . On Earth, most of the volatile sulfur resides in the ocean as sulfate ions. The presence of this large amount of  $\text{SO}_2$  in the atmosphere is responsible for the production of a dense  $\text{H}_2\text{SO}_4$  cloud on Venus. Third, the atmosphere of Venus contains large amounts of HCl. On Earth, the bulk of chlorine is in the form of salt (NaCl) in the oceans.

## 8.2 Atmospheric Chemistry and Atmospheric Evolution

It is now generally accepted that the origin of water in the planets is dehydration of hydrous minerals during formation. The bulk of infalling material has composition similar to that of CI chondrites, which contain up to 3 wt%  $\text{H}_2\text{O}$ . Once the accreting planetary body exceeds a critical size, impact velocities become sufficiently high that devolatilization can start. The critical radii,  $R_1$ , for Earth, Venus, and Mars are about 20%, 20%, and 40% of their present radii, respectively. Complete devolatilization can occur when the planets grow to another critical radius,  $R_2$ . The values for  $R_2$  are roughly 50% of the present radii for the Earth and Venus; Mars never reached  $R_2$ . This implies that the terrestrial planets all should have acquired massive amounts of water of the order of terrestrial oceans. Why, then, is the ocean of water absent from Venus?

In a seminal paper, *Ingersoll* [1969] showed that water vapor could have been a major constituent in the atmosphere of Venus, and that photolysis of  $\text{H}_2\text{O}$ , followed by hydrogen escape could approach the UV photon limit of about  $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ . Under such conditions, an amount of water equivalent to the terrestrial ocean could be lost in 100 Myr.

Evidence that the atmosphere of Venus has lost most of its water (assuming it had acquired a large quantity) came from the Pioneer Venus measurements of the D/H ratio, which is about 100 times the terrestrial value [*McElroy et al.*, 1982; *Donahue et al.*, 1982] and has been confirmed by Earth-based spectroscopy [*de Bergh et al.*, 1991]. This implies that Venus has likely lost at least the equivalent of 100 times more water than its present reservoir. The loss of hydrogen from Venus is determined by the efficiency of the escape processes and the rate at which hydrogen is transferred from the lower atmosphere to the upper atmosphere where the escape processes operate [*Gurwell and Yung*, 1993]. *Kasting and Pollack* [1983] suggested the early escape of hydrogen from Venus could have been a hydrodynamic process rather than kinetic evaporation from the exosphere, similar to that proposed for Pluto [*Krasnopolsky*, 1999; *Tian and Toon*, 2005]. However, there was no direct observational evidence for hydrodynamic escape from a planetary atmosphere until the recent observation of H atoms escaping from the extra-solar planet HD209458b [*Vidal-Madjar et al.*, 2003]. *Liang et al.* [2003] showed that the source of the H atoms that fuel the hydrodynamic escape on this planet is photolysis of  $\text{H}_2\text{O}$ . This process could have been the same as the one postulated by *Ingersoll* [1969] for the atmosphere of Venus.

The above interpretation is by no means unique. There is an alternative view of the evolutionary history of water on Venus. According to *Grinspoon and Lewis* [1988], Venus lost all its initial inventory of water very early. The current water vapor content is the result of a balance between supply by cometary impact and loss processes. *Grinspoon* [1993] argued that another recent source of water might have been the massive outgassing from catastrophic resurfacing of the planet in the past 0.5–1 Gyr. Determination of noble gas isotopic abundances for Venus may help constrain the relative importance of external versus internal sources of volatiles, but the interpretation of such measurements has often been contentious. Resolution of these two different evolutionary models may depend on an accurate determination of the present escape flux of H and D from Venus [*Donahue*, 1999; *Lammer et al.*, 2006].

The D/H ratio in water vapor on Mars also is enhanced, but by a factor of 6 [*Owen et al.*, 1988; see also *Krasnopolsky et al.*, 1997], which implies that Mars also may have lost large amounts of water in the past [*Yung et al.*, 1988; *Kass and Yung*, 1995; 1999; *Cheng et al.*, 1999; *Miller and Yung*, 2000]. This enrichment of D over H is largely the result of photochemical processes that preferentially dissociate  $\text{H}_2\text{O}$  relative to HDO and the lower efficiency for the escape of D relative to H at the exobase (where the atmosphere merges into space). In addition, *Fouchet and Lellouch* [2000] and *Bertaux and Montmessin* [2001] point out that there is a trap

for deuterium on Mars due to water vapor condensation. The latter authors name this the “deuteropause”, by analogy with the tropopause in the terrestrial atmosphere [Moyer *et al.*, 1996; Kuang *et al.*, 2003]. One implication of these theories about Mars’ evolution is that Mars must have been warmer in the past, which implies it was more likely to have been habitable. However, it is currently impossible to determine the precise amount of water that has escaped in the past. Estimates of the lost water range from lower values of 9 m [Kass and Yung, 1999] and 14 m [Jakosky, 1990] to higher values of 65 to 120 m [Krasnopolsky, 2000].

It is a remarkable fact that the Earth has remained habitable throughout its planetary history even though the solar luminosity has increased substantially. The major energy source for the solar system is the sun. The sun’s luminosity has gradually increased by about 40% since the origin of the solar system. The reduced solar constant during the nascent period of the Earth would imply that the planet was completely frozen, a result in conflict with known geological evidence (e.g., sedimentary rocks). A resolution of this paradox is to postulate that the CO<sub>2</sub> content of the atmosphere has been changing with time to compensate for the changing solar constant. According to the Gaia hypothesis, the biosphere may indeed have evolved since its origin to counteract the problem of the increasing luminosity of the sun. However, there is a finite limit to the power of Gaia. The abundance of CO<sub>2</sub> is now very low, while the luminosity of the sun continues to increase. Further decrease of CO<sub>2</sub> by biological activity may be difficult because photosynthesis itself stops when the CO<sub>2</sub> mixing ratio falls below a threshold level of about 150 ppmv. Thus, there is a point beyond which the Gaian control of the global environment would fail and the Earth would become Venus-like in 30–300 Myr [Lovelock and Whitfield, 1982]. Venus may be the ultimate graveyard of all terrestrial planets above a certain critical size.

### 8.3. Implications of Venus Clouds and Chemistry for Studies of Extra-Solar Planets

NASA is undertaking a major effort to find terrestrial planets around other stars. A hope is that they may resemble Earth. A likely possibility from the present state of the solar system, and from the increasing luminosity of the Sun, is that some significant fraction of these terrestrial planets will resemble Venus. Many of the observable characteristics of a terrestrial planet resembling Venus are determined by its atmospheric chemistry and clouds. The first observations will not resolve an extra-solar planet: its global brightness, variability and spectrum will be the first measurements. The mass, radius and albedo can also be inferred from the

observations. It is important to remember that the observed temperature may differ from the effective temperature and also from the surface temperature. Venus provides an excellent example in our own solar system.

The distinctive characteristics of Venus would be clear to the first observations from another solar system:

1. High albedo with blue and UV broadband absorption.
2. CO<sub>2</sub> atmosphere, detectable from CO<sub>2</sub> absorption bands and CO emissions.
3. Lack of water, from absence of H<sub>2</sub>O absorption bands and OH emission.
4. Clouds of H<sub>2</sub>SO<sub>4</sub>, inferred from SO<sub>2</sub> absorption bands.
5. In the UV, Venus’ brightness will vary over the 4-day super-rotation of the cloud-top markings.

Thus, Venus-like planets could be clearly distinguished from potentially habitable Earth-like planets. The models we have developed for Venus’ clouds and chemistry (along with the coupled radiation and dynamics) provide a starting point for understanding those planets. Since our evolutionary models of Venus may encompass Earth’s future evolution, this may allow inferences about whether Venus-like planets around other stars ever *were* habitable, and thus to examine the effects of the runaway greenhouse in other solar systems.

## 9. RECOMMENDATIONS AND FUTURE DIRECTIONS

Better observations of atmospheric composition, including vertical, horizontal, and temporal variations are required to advance our understanding of Venus’ clouds and chemistry.

1. The most critical observation required for understanding the chemistry of the middle atmosphere is a determination of the ground-state O<sub>2</sub> abundance. Venus Express will not provide this, but high resolution (resolving power ~ 400,000) ground-based spectra might determine its column abundance.
2. Vertical profiles of the time-varying O<sub>2</sub>(<sup>1</sup>Δ) airglow emission from Venus Express will constrain models of the oxygen airglow chemistry and limit the range of acceptable models.
3. The most direct observational test of the proposed chlorine chemistry would be detection of ClC(O)OO, which may be possible now that its structure and spectroscopy are known [Pernice *et al.*, 2004]. Observing O<sub>3</sub>, COCl<sub>2</sub>, ClO, or Cl<sub>2</sub> would provide important indirect tests of models. It is not clear whether Venus Express can observe these compounds, but simulations indicate a submillimeter spectrometer, such as that proposed for the *Vesper* mission could measure the abundances of ClO, O<sub>2</sub>(<sup>1</sup>Δ), and O<sub>2</sub>

even if their concentrations are a factor of 10 smaller than predicted by recent global-average models [Pernice *et al.*, 2004; Mills *et al.*, 2006]. The O<sub>3</sub> abundances predicted by these recent models should also be detectable by *Vesper*'s submillimeter spectrometer.

4. Direct observational tests of sulfur chemistry will be provided by three-dimensional maps of SO<sub>2</sub>, SO, H<sub>2</sub>S (if present and observable), and OCS derived from Venus Express spectroscopy and VMC images.

Better observations of cloud particle properties and their variation also are required. The size distribution, shape, and composition of the majority of the aerosol mass are still open, despite our assurance that "mode 2" (the aerosols visible at the cloud tops) are spherical droplets of concentrated sulfuric acid. Venus Express will make remote measurements of the clouds. Multiple observations will be combined to improve our understanding. Key tasks are to compare, reconcile and consolidate these measurements.

The information expected from Venus Express also should justify more detailed studies of the interactions among radiation, clouds, chemistry and dynamics. For example,

1. Simultaneous three-dimensional maps of time-varying temperatures and the abundances of CO and other species will permit development of multi-dimensional chemical transport models.
2. Spatially-resolved observations of H<sub>2</sub>O are needed to understand the large temporal variations reported in ground-based studies [Sandor and Clancy, 2005] and to refine our understanding of the cloud layers.

Determination of the mineralogy on the surface of Venus is needed for significant progress on understanding the chemical interaction between the atmosphere and surface and how this interaction may have changed over the course of Venus' evolution.

The most important laboratory measurement needed for understanding the chemistry in the Venus middle atmosphere is a more accurate determination of the equilibrium constant for ClCO and any temperature dependence. Verification of the rate for Reaction (29) which forms ClC(O)OO and an assessment of its uncertainties is also needed. Laboratory measurements are also required to assess whether more speculative schemes for oxidizing CO, such as heterogeneous reactions, are sufficiently rapid. Finally, laboratory spectra and in situ measurements will be the only means by which the unknown UV absorber can be definitively identified. Spectra do not exist for many of the proposed candidates, so it is not possible to compare model calculations with observations.

For the lower atmosphere's chemistry, the validity of reactions (15), (16), (17), and (18) needs to be ascertained in laboratory studies. Laboratory work also is needed to deter-

mine whether equivalent heterogeneous reactions are more important than these gas-phase reactions. Further modeling may be required to identify alternative chemical schemes, particularly if any of these reactions is found to not occur or to be too slow to explain observations.

The discovery of NO in the cloud layers presents the exciting possibility that heterogeneous chemistry on the surface of sulfate aerosols may convert the reservoir species of chlorine into active species, which can then participate in catalytic chemistry. The reservoir species (HCl, ClONO<sub>2</sub>) are chemically unreactive, but the labile species can readily participate in catalysis. These reactions have been shown to play a major role in the destruction of ozone in the Earth's atmosphere [Solomon *et al.*, 1997].

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