ACS EARTH AND SPACE CHEMISTRY

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Thermodynamic Constraints on the Lower Atmosphere of Venus

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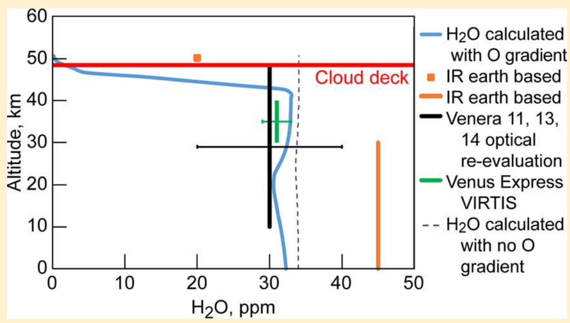
ABSTRACT: The lower Venusian atmosphere is the region from the surface to the cloud deck or about 0−50 km. Early modeling studies of the atmosphere were primarily based on thermodynamics; more recent modeling studies are based on kinetics of the elementary reactions. In this paper, we take the accepted nominal composition of near-surface gases at ∼42 km and show some of the constituents are indeed at thermodynamic equilibrium. We impose a small oxygen gradient and use a thermodynamic free energy minimization code to describe the vertical gradients of mixing ratios for the primary gases in the lower atmosphere. The oxygen gradient is within the measurement errors on oxygen and thus preserves mass conservation. Reasonable agreement is found between our calculations and the vertical profiles of H_2O, H_2SO_4, OCS, H_2S, and S_n (n = 1−8). We then did a kinetic analysis of kinetic expressions for the formation of these species. Consistent with other investigators, we find that very few if any reactions should be at equilibrium in the lower atmosphere. Yet our equilibrium calculations do show some agreement with observations. We conclude that the available kinetic expressions likely need improvement and factors such as catalysis must be included to reflect actual Venus conditions.



KEYWORDS: *Venus atmospheres, thermodynamic modeling, kinetic modeling, lower Venusian cloud deck, sulfuric acid formation*

1. INTRODUCTION

Our knowledge of the Venusian atmosphere is continually developing from probe data, earth-based observations, and models. Actual measurements of the composition of the lower atmosphere of Venus are complex due to the cloud layer. Much of our data comes from the Venera, Vega, and Pioneer Venus probes descending through the cloud layer into the atmosphere. The Magellan probe gave important information on cloud layer. More recently Venus Express and earth-based observations have contributed to our knowledge of the Venus atmosphere. Many of these measurements are of remarkable fidelity but issues such as instrument contamination must always be considered.[1] In 1984, near-infrared windows were found in the cloud layer,[2] which has since enabled earth-based observations. There are numerous reports of the lower atmosphere composition in the literature. Notable reviews include those of Hoffman et al.,[1] von Zahn et al.,[3] de Bergh et al.,[4] Bézard and de Bergh,[5] and Krasnopolsky and Lefèvre.[6] Tables 1 and 2 summarize the data we have used in this study.[4,7−29] Below we briefly summarize the findings and issues for SO_2, H_2O, CO, OCS, H_2S, S_n (n = 1−8), and H_2SO_4 in the lower atmosphere. All data are in parts per million by volume (ppmv).

Received: June 14, 2017
Revised: August 2, 2017
Accepted: August 4, 2017
Published: August 4, 2017

DOI: 10.1021/acsearthspacechem.7b00067
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

Table 1. Lower Atmosphere Mixing Ratios of Gases on Venus

species	elevation (km)	conc (ppm)	method and reference
SO_2	12	25 ± 2 (ISAV 1)[a] 20 (ISAV 2)	Vega 1 and 2 UV Spectroscopy[7]
SO_2	22	38 (ISAV 1) 38 (ISAV 2)	Vega 1 and 2 UV Spectroscopy[7]
SO_2	42	125 (ISAV 1) 140 (ISAV 2)	Vega 1 and 2 UV Spectroscopy[7]
SO_2	52	150 (ISAV 1) 65 (ISAV $_2$)	Vega 1 and 2 UV Spectroscopy[7]
SO_2	21.6	185 ± 43	Pioneer Venus Gas Chromatograph[8]
SO_2	41.7	>176	Pioneer Venus Gas Chromatograph[8]
SO_2	51.6	<600	Pioneer Venus Gas Chromatograph[8]
SO_2	4_2	130 ± 40	Earth Based IR[9]
SO_2	42	180 ± 70	Earth Based IR[10]
SO_2	30−45	140 ± 37 (2009 obs)[b] 126 ± 32 (2010 obs)	Earth Based IR[11]
SO_2	30−40	130 ± 50	Venus Express VIRTIS[12]
H_2O	48.4 (cloud base)	20	Earth Based IR[13]
H_2O	30 to surface	45	Earth Based IR[13]
H_2O	10−48	30 ± 10	Venera 11, 13, 14 Optical Spectra (re-evaluation)[14]
H_2O	clouds	30−50	Venera 11, 13, 14 Optical Spectra (re-evaluation)[14]
H_2O	10−40	30 ± 10	Earth Based IR[10]
H_2O	30−40	31 ± 2	Venus Express VIRTIS[12]
H_2O	30−40	(22−35) ± 4	Venus Express VIRTIS[15]
CO	51.6	32.2	Pioneer Venus Gas Chromatograph[8]
CO	41.7	30.2 ± 18	Pioneer Venus Gas Chromatograph[8]
CO	21.6	19.9 ± 3.15	Pioneer Venus Gas Chromatograph[8]
CO	30	23 ± 5	Earth Based IR[4,10,16]
CO	40	29 ± 7	Earth Based IR[4,10,16]
CO	42 to surface	28 ± 14	Venera 12 Gas Chromatograph[17]
CO	35	22 (equator) 37 (pole)	Venus Express VIRTIS[18]
CO	36	24 ± 3 to 31 ± 2	Venus VIRTIS[12]
CO	36	24 ± 2	Earth Based IR[19]
CO	35	25 ± 3 (2009 obs) 22 ± 2 (2010 obs)	Earth Based IR[11]
OCS	33	(2.5−4) ± 1	Venus Express VIRTIS[12]
OCS	65	0.3−9 ppb	Earth Based IR[20]
OCS	33	4.4 ± 1.0	Earth Based IR[10]
OCS	30 36	5−20 0.55 ± 0.15	Earth Based IR[19]
OCS	36	0.44 ± 0.10 (2009 obs) 0.57 ± 0.12 ($_2$010 obs)	Earth Based IR[11]
H_2S	<20 km	3 ± 2	Pioneer Venus Mass Spectrometry[21]
H_2S	21.7	<2	Pioneer Venus Gas Chromatograph[8]
S_{1-8}	<50	20 ppb	Venera 11, 12 Spectrophotometers[22]
S_3	3−10	11 ± 3	Venera 11 Spectrophotometer[23,24]
	10−19	18 ± 3	Venera 11 Spectrophotometer[23,24]
S_4	3−10	4 ± 4	Venera 11 Spectrophotometer[23,24]
	10−19	6 ± 2	Venera 11 Spectrophotometer[23,24]
H_2SO_4	38−52	0−18 (equator)	Mariner 10 Radio Occultation[25,26]
H_2SO_4	38−52	0−7 (67°N)	Mariner 10 Radio Occultation[25,26]
H_2SO_4	50−52	1−5 (0−70°S)	Venus Express[27]

[a]ISAV refers to the spectrometer. [b](2009 obs) means observation in 2009.

Table 2. Lower Cloud Bottom Altitude

lower cloud bottom altitude (km)	method
47	Magellan[28]
48.4 ± 0.75	Pioneer Venus[28]
48.4	calculated from kinetics of H_2SO_4 production[28]
48.4	Yung and DeMore Model C[29]

The major sulfur carrier is SO_2 and most data at low elevations are from the Vega 1 and 2 probes.[7] This SO_2 gradient is controversial[5] as it indicates decreasing SO_2 levels near the surface, which are not expected. There is no clear gas-phase reaction for consuming SO_2 in the lower atmosphere.

Nonetheless, the Vega 1 and 2 measurements are among the only near surface measurements we have of SO_2 and there is no reason from the actual instrument to doubt them. Minerals on the surface may act as a sink for SO_2 and reduce its concentration at lower elevations. One possible sink is the well-known calcite/anhydride reaction at the surface[30,31]

$$CaCO_3(s) + SO_2(g) = CaSO_4(g) + CO(g) \quad (1)$$

Note that this reaction alone provides a source of CO at the surface. Other sources of CO in the lower atmosphere must provide the observed increase in CO with elevation, as will be discussed. Fegley and Prinn[30] have shown the rate for reaction 1 is about one micrometer of $CaSO_4$ per year and it is possible that aeolian weathering by one meter per second winds would remove this anhydride layer to expose fresh calcite for reaction. Carbonate may be present in carbonatite lavas on Venus.[32] On the upper side of the lower atmosphere, a discussion of possible UV absorbers in the cloud layer suggests that SO_2 decreases through the cloud layer.[33] Understanding the presence or absence of a decreasing SO_2 gradient is important and more observations are needed here.

The other complication with SO_2 levels is the observed temporal variation, which has been attributed to volcanism.[30,34−36] The accepted "nominal value" for SO_2 of 150 ppm may represent a high point in a cycle. However, more data is needed to definitively prove this.

There are a large number of probe and earth-based measurements of H_2O. The early probe data (Vega, Venera, and Pioneer Venus) on H_2O is somewhat contradictory showing variations from 20 to 5000 ppm.[8,10] This appears to be resolved by the earth-based observations, which give values in the 20−40

DOI: 10.1021/acsearthspacechem.7b00067
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

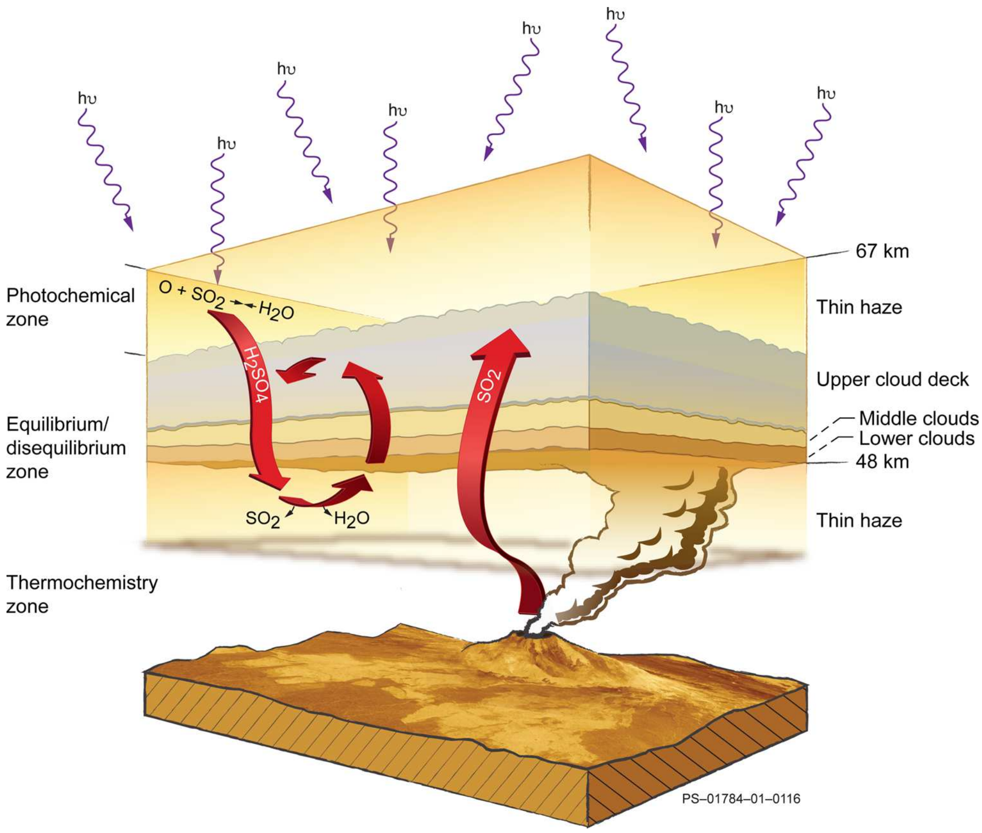


Figure 1. Schematic of Venusian atmosphere, showing the three zones as defined by Mueller.[40] The boundaries between the zones depend on the particular species. Adapted from Grinspoon.[41]

ppm range below the cloud layer and seem to be constant with elevation. Some Venera 11−14 and Pioneer Venus data indicates a decrease in water vapor concentration from the surface to 10 km, a constant level to near the lower cloud bottom altitude, and then another decreasing gradient to the lower cloud bottom, due to sulfuric acid formation.[37] There seems to be general agreement that the water vapor mixing ratio is 30 ± 10 ppm from 5 to 40 km.[5]

The data from the probes and earth-based observations of CO is reasonably consistent. De Bergh et al.[4] point out that there appears to be some variation in CO with latitude. This is indicated by an ~35% increase toward northern latitudes. de Bergh et al.[4] also discuss likely temporal variations of CO. However, there is agreement that CO concentration decreases toward the surface.

As discussed by de Bergh et al.,[4] OCS was detected by Venera 13 and 14 in the lower atmosphere, but not by Pioneer Venus. Earth-based observations have clearly detected OCS. The mixing ratio appears to increase at 25−45 km and is likely related to the decrease in CO in this same elevation range.[4,10,12] The most obvious way to explain the opposing gradients of CO and OCS is the consumption of CO to form OCS[38]

$$CO(g) + 1/2S_2(g) = OCS(g) \tag{2}$$

After 25−30 km, the OCS mixing ratio is constant at about 0.1 ppm to the surface.[12]

There are only limited data on other sulfur-bearing gases. Data on H_2S are from the Pioneer Venus mass spectrometer and gas chromatograph.[1,8] Several sulfur allotropes, for example, S_3 and S_4, have also been detected by the Venera 11 and 12 probes but at very low levels.[23,24]

Sulfuric acid, H_2SO_4, is of primary interest as aerosols of sulfuric acid form the clouds. H_2SO_4 forms as a vapor a few kilometers below the clouds and then as a liquid at the cloud deck.[39] Radio occultation measurements[25,26] have measured H_2SO_4 amounts in the cloud layer. The mixing ratio depends on the latitude with the largest amount at the equator. The Pioneer Venus probe conducted nephelometer measurements for the lower cloud bottom altitude.[28] This elevation has also been predicted with remarkable fidelity by several investigators.[28,29] Table 2 lists these measured and calculated lower cloud bottom altitudes.

There are several models of the lower atmosphere of Venus, involving both thermodynamics and kinetics. Mueller[40] first divided the atmosphere into three vertical layers. The gases at the lowest elevations likely exhibit some degree of chemical equilibrium, the intermediate region is a mix of gases at chemical equilibrium and disequilibrium, and the gases at the upper region are described by photochemical reactions. Figure 1 schematically illustrates these regions.[41]

This three region view maintains acceptance, although the boundaries change as we learn more about the Venusian atmosphere.[42] Furthermore, the exact boundaries between these regions are controversial and dependent on the particular gas and governing reaction(s). During the 1980s, a number of thermochemical models were published on the lower atmosphere.[43−45] These utilized a free energy minimization computer code to determine the expected equilibrium mixture. The calculations reproduce some of the observations of probes in that era.

DOI: 10.1021/acsearthspacechem.7b00067
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

Krasnopolsky[28,35,46] points out that thermodynamics cannot fully explain the observations. Further he shows that some reactions in the lower atmosphere are kinetically limited, such as

$$3CO(g) + SO_2(g) = 2CO_2(g) + OCS(g) \qquad (3)$$

Measured SO_2/OCS ratios are compared to equilibrium calculations. There is only agreement at temperatures above 700 K, which corresponds to the lowest 5 km of the Venusian atmosphere. Thus, for this reaction one cannot assume chemical equilibrium. Fegley et al.[47] have also shown that thermodynamic equilibrium for all species is only possible in the lowest elevations. They do a kinetic analysis of the principle CO consuming reactions and show that these are only feasible at the lowest elevations. Zolotov[48] discusses equilibrium in the lowest layers of the Venus atmosphere. He points out that the higher temperatures and the possible catalytic effects of the surface minerals make equilibrium among the gases most likely in the near surface region.

The nominal atmosphere of Venus is given in Table 3.[49] The composition of this atmosphere as a function of altitude has been modeled by several investigators.[35,39,50,51] Mills, Esposito et al.[50] point out there are three primary chemical cycles,the CO_2 cycle, sulfur oxidation cycle, and polysulfur cycle. The CO_2 cycle involves photon-assisted dissociation of CO_2 to CO and O and is fairly well understood. The sulfur oxidation cycle is illustrated in Figure 1 and involves the formation of H_2SO_4 in the upper cloud layer and decomposition of H_2SO_4 in the lower cloud layer. The polysulfur cycle involves the minor sulfur species and is less well understood. These reactions have all been modeled with coupled chemical kinetic expressions.

Table 3. Nominal Composition of Venusian Atmosphere from Reference 49 and References Therein

gas	abundance	elevation	thermodynamic equilibrium (42 km, 410 K, 2.8 bar)
CO_2	96.5 ± 0.8%		96.48%
N_2	3.5 ± 0.8%		3.5%
SO_2	150 ± 30 ppm	22–42 km	138 ppm
H_2O	30 ± 15 ppm	0–45 km	33 ppm
Ar	70 ± 25 ppm		
CO	30 ± 18 ppm	42 km	1.8×10^{-5} ppm
He	12 ± 8 ppm		
Ne	7 ± 3 ppm		
OCS	4.4 ± 1 ppm	33 km	0.05 ppm
H_2S	3 ± 2 ppm	<20 km	0.03 ppm
HDO	1.3 ± 0.2 ppm		
HCl	0.6 ± 0.12 ppm	cloud top	0.6 ppm
Kr	~25 ppb		
S_n (n = 1–8)	20 ppb		
HF	5 ppb	cloud top	5 ppb
Xe	~1.9 ppb		

Thus, the early modeling work for the lower atmosphere centered on thermodynamic modeling and most of the later work centered on kinetic modeling. Nonetheless, thermodynamic modeling may still be useful as a partial description of the lower Venusian atmosphere. As noted, some of the early thermodynamic modeling did in fact reproduce some of the actual Venusian atmosphere observations. Further, other factors such as high ambient pressure and atmospheric particulates (possible catalysts) may push the reactions closer to equilibrium. Thermodynamics also establishes limits of a reaction.

More recently, some constituent behavior in the lower atmosphere has been described with thermodynamics.[52] A small gradient in oxygen is introduced to describe the SO_2 profile measured by the Vega 1 and 2 UV spectrometers. Imposing this oxygen gradient together with thermodynamic calculations successfully describes the following features of the lower atmosphere: increase of SO_3 and H_2SO_4 near the cloud base, decrease in H_2O near the cloud base, and decrease in OCS near the surface. The thermodynamic modeling does not describe the CO behavior. These calculations were done using the IVTAN thermodynamic database and free energy minimizer.[53]

The above reference[52] is only a short conference abstract. This study represents a combined effort by the group at NASA Glenn and Washington University to revisit and expand on the original calculations. With a small oxygen gradient, we are able to reproduce several important features of the lower atmosphere with equilibrium calculations. We then conduct a kinetic analysis and show that many of the elementary reactions are predicted to not attain equilibrium. This apparent contradiction indicates the need for better kinetic data in conditions similar to Venus.

2. METHOD OF THERMODYNAMIC CALCULATIONS AND KINETIC ANALYSES

We use the FactSage free energy minimizer and associated databases.[54] The databases used in FactSage are taken from a variety of sources but many of the compounds of interest, particularly the important sulfur compounds, are taken from the JANAF tables.[55] The nominal composition of the Venusian atmosphere is given in Table 3 and converted to elemental abundances, shown in Table 4. We took the SO_2 mixing ratio at 42 km for the nominal composition and this corresponds to 410 K and 2.8 bar from the VIRA profile.[56] As an initial calculation, we ran the elemental abundances for the nominal composition in the free energy minimizer. The results are shown in the third column of Table 3. Note that the calculated values for CO_2, N_2, SO_2, H_2O, HCl, and HF are in close agreement to nominal values in the second column. However, the calculated values for OCS and H_2S are off and the calculated CO values are dramatically off. This first calculation indicated that thermodynamics may describe some of the atmospheric chemistry whereas other constituents might be better described with kinetics. In the next section, we impose a small oxygen gradient, as described below.

Table 4. Elemental Composition in Numbers of Atoms

element	number from nominal composition	number with imposed gradient
O	1,930,351.4 ± 15791.4	1,929,992 to 1,930,449.043
C	965021.4 ± 7722	965021.4
N	70,000 ± 560	70,000
S	157.4 ± 32	157.4
H	66.6 ± 36.12	66.6
Cl	0.6 ± 0.12	0.6
F	0.005	0.005

Our approach here is to introduce a small gradient in oxygen and conduct calculations at each elevation. Because oxygen combines with carbon, sulfur, nitrogen, or hydrogen this small gradient would be manifest in a gradient of an observed gas such as CO_2 or SO_2. The temperature and pressure of each elevation is set by the VIRA profile.[56] As done in the original Fegley and Schaefer[52] study, we derived this gradient from the Vega 1 and 2 SO_2 measurements. As noted in the Introduction, this gradient is controversial but at this point we have no other low elevation

DOI: 10.1021/acsearthspacechem.7b00067
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

data. The derived oxygen gradient is shown in Figure 2a in a plot of elevation versus number of oxygen atoms. Note the gradient is

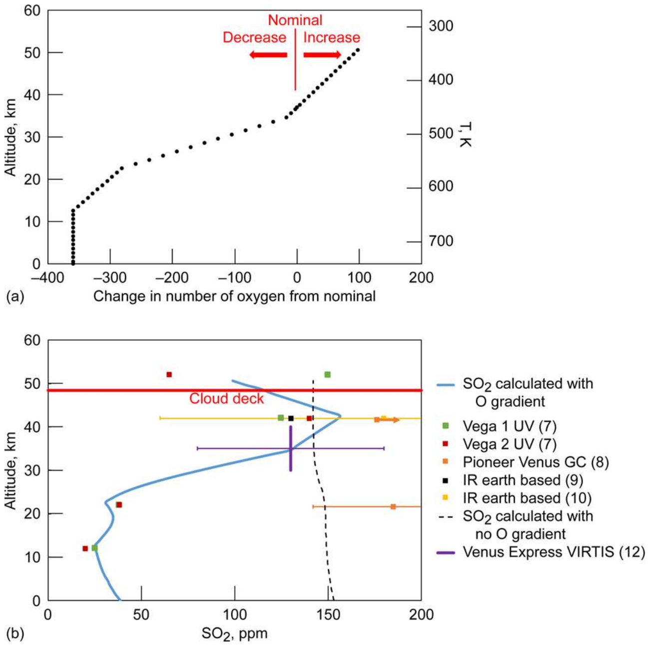


Figure 2. Gradient in oxygen (a) as developed from SO_2 profile (b). The calculated SO_2 gradient with and without an oxygen gradient is shown in (b). The arrow indicates a lower limit.

within the errors on number of oxygen atoms, as given in Table 4. Thus, mass conservation within these error limits is maintained. The small addition/removal of oxygen atoms is manifest in small changes in CO_2, SO_2, and the other oxygen bearing gases. We use the VIRA profile of temperature and pressure as a function of elevation together with the oxygen gradient. Calculations are conducted in steps of one kilometer through the lower atmosphere. Figure 2b shows the SO_2 gradient calculated with and without the imposed oxygen gradient. As expected, the latter is nearly constant.

The origin of the oxygen gradient may be due to a variety of factors. There may be a sink for some of the species such as CO_2 and SO_2 at the surface.[30,38] To understand this, we need more information on the surface composition and extent of magmas and other possible sinks. It is also likely that photochemical dissociation of CO_2 in the cloud layer may produce more O in the upper regions.

In the second part of this study, we try to reconcile the thermodynamic results with reported kinetics for some of the elementary reactions. Following the methods of other investigators[46,47] we compare the mixing lifetime (t_{mix}) to the chemical lifetime (t_{chem}). Unless $t_{chem} < t_{mix}$, the gases will diffuse to higher elevations and colder temperatures (quench) before they react. The mixing lifetime is defined as

$$t_{mix} = \frac{H^2}{K_{eddy}} \tag{4}$$

Here, H is the pressure scale height (16 km at 735 K) and K_{eddy} is a parametrized eddy diffusion coefficient, which is taken as 10^4–10^6 cm^2/sec. This gives a t_{mix} of 0.08–8.2 earth years. Chemical lifetime for a particular species is simply the time it takes for consumption of that species. It is calculated from the rate expression. For a bimolecular reaction of $A + B$, the chemical lifetime for A is defined as

$$t_{chem} = \frac{[A]}{\left(\frac{d[A]}{dt}\right)} = \frac{[A]}{k[A][B]} = \frac{1}{k[B]} \tag{5}$$

Here, k is the tabulated rate expression for the particular reaction and $[B]$ is concentration of species B which we take as the calculated equilibrium concentration as a first approximation.

For a termolecular reaction, the expression includes another reactant concentration. Generally an error band of 2–3 times is taken on rates calculated in this manner.

3. GASES IN LOWER ATMOSPHERE

The Venusian surface is known to be 740 K at 92 bar pressure, which is in the supercritical fluid region of the CO_2 phase diagram. This is such a high temperature that the supercritical phase is generally more "gaslike" in properties. So the surface has been regarded as a dense, high-pressure gaslike mixture of CO_2, N_2, and other minor gas constituents. However, a recent study[57] proposes that the supercritical fluid may account for the observed instability in the lowest 7 km and create a region of nearly all CO_2 in these lowest layers. More data is needed to confirm or refute this.

Using the imposed oxygen gradient, we calculated the vertical profiles for the gases H_2O, CO, OCS, H_2S, S_n, and H_2SO_4 (Figures 3–8). These figures also include most of the data with

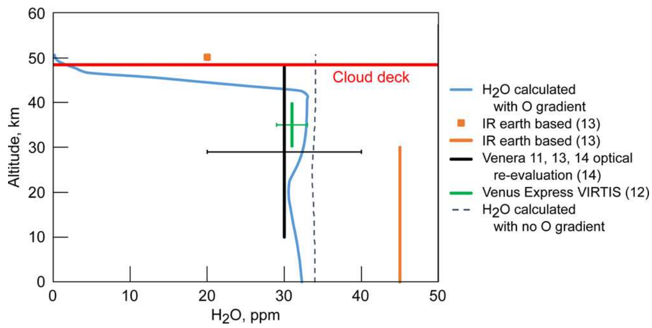


Figure 3. Calculated H_2O concentration compared to observations.

error limits in Table 1. We also calculated the first appearance of H_2SO_4 liquid, which is the cloud deck boundary. For H_2O, CO, OCS, and H_2S profiles, we show the calculation with and without an oxygen gradient.

Figure 3 gives calculated H_2O concentrations. Generally, these compare favorably with the observations. As noted in the Introduction, most of the data suggest a constant H_2O level with elevation. Kinetic modeling of the lower atmosphere[28] also leads to constant H_2O levels of 20–25 ppm. Above about 42 km, the H_2O levels decrease too fast in this analysis. Thermochemically this occurs because of the reaction of SO_3 and H_2O to form H_2SO_4. However, kinetic models require some H_2O to exist in the cloud layer.[58] Venus Express measurements in the cloud layer indicate several ppm, for example 1 ppm of H_2O at 70–110 km[59] and 6.1 ± 1.2 ppm of H_2O at 61.9 ± 0.5 km and low latitudes.[60] Thus, H_2O formation within the cloud layer cannot be described with thermodynamics and is likely photochemically assisted.

Figures 4 and 5 show the results for CO and OCS. The initial calculations (Table 3, column 3) indicate that CO cannot be calculated from thermodynamics. This is also evident in Figure 4. CO is likely formed via photon-assisted dissociation of CO_2 in

DOI: 10.1021/acsearthspacechem.7b00067
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

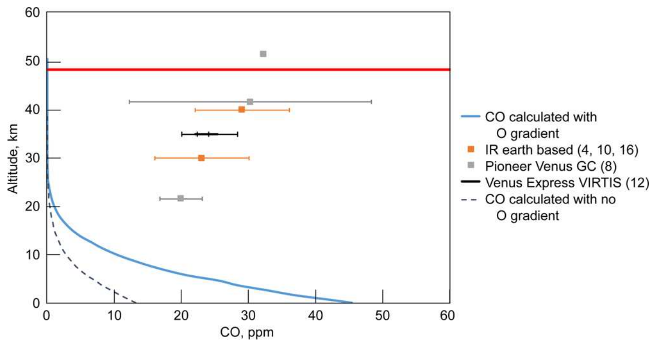


Figure 4. Calculated CO concentration compared to observations. See Table 1 for more details of the Venus Express data.

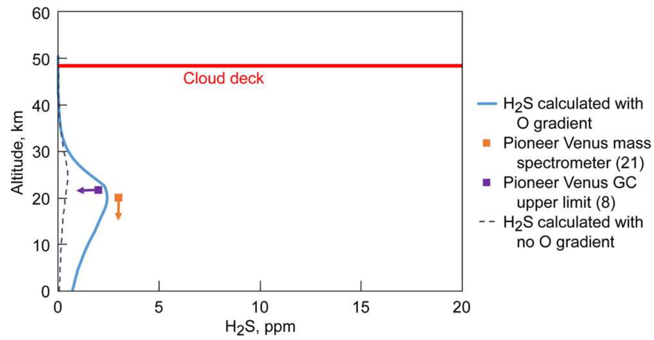


Figure 6. Calculated H_2S concentration compared to observations. The arrows indicate upper limits.

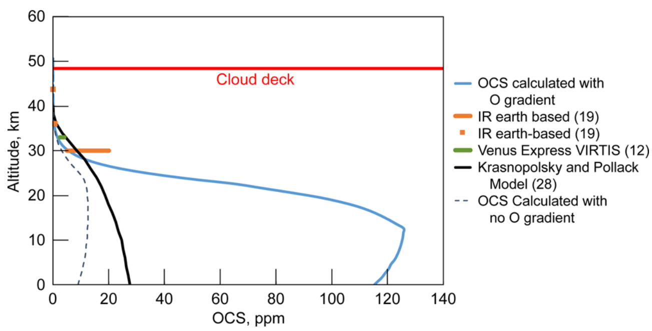


Figure 5. Calculated OCS concentration compared to observations.

the upper atmosphere (eq 4). Thermodynamics suggests that the amount of CO should increase at the higher temperatures near the surface.[42] However, the data in Figure 4 shows that the measured amounts of CO decrease. A re-evaluation of the surface measurements of the CO concentration from the CONTRAST experiment indicate [CO] ranges from ≥2.3 to ≥6.8 ppm.[42] As noted, a primary source of CO is

$$CO_2(g) + h\upsilon \rightarrow CO(g) + O(g) \qquad (6)$$

In the lower atmosphere the smaller amount of energetic photons supports the observation that this reaction is less likely to occur.

Fegley et al.[47] methodically examined the elementary reactions involving CO and CO_2 and show that the chemical time constant is greater than the convective mixing time constant. This means that before the gases can equilibrate at the lower (hotter) elevations, they will move to higher (cooler) elevations, where equilibrium is not attained.

There is agreement on a drop of OCS at ∼30 km.[61] As shown in Figure 5, thermodynamic calculations with the oxygen gradient do not capture this. Figure 5 does show agreement with OCS observations at higher elevations.

Figure 6 shows the results for H_2S calculations. The data for H_2S is limited but seems to be in the ppm range primarily. The calculations are reasonably close to the data at 20 km but more measurements are needed to determine if thermodynamics can describe the variation of this gas with elevation. The calculation in Figure 6 without an oxygen gradient gives similar results to that with an oxygen gradient. It appears the calculations with an oxygen gradient are closer to the measured numbers but given the error probably both are close.

The data on the allotropes of sulfur gas is limited. The most common allotrope observed at lower elevations seems to be S_3 as predicted by thermodynamics. Maiorov et al.[23] have interpreted the spectrophotometric data from Venera 11, 12 to give mixing ratios in the ppb level or less. These are shown along with the thermodynamic calculations in Figure 7.

An examination of the FactSage output for the first appearance of liquid H_2SO_4 as temperature and pressure are changed gives the dewpoint and the boundary of the cloud layer. These results are shown in Figure 8. Note the concentration of H_2SO_4 vapor agrees reasonably well with radio occultation measurements[25,26] at the equator. The first liquid H_2SO_4 appears at 51.6 km, which is in reasonable agreement with measurements and other calculations of the cloud deck elevation (48.4 km). However, this is only H_2SO_4 liquid, and there does not seem to be enough water for the hydrated forms of H_2SO_4 to appear.

The formation of the sulfuric cloud aerosols is, of course, more complex and cannot be described by thermochemistry alone. Parkinson et al.[62] have summarized the 1D models for this as follows. The sulfuric acid forms at the higher cloud elevations and migrate downward (sedimentation). At lower elevations and higher temperatures, they vaporize and create the H_2SO_4 liquid/vapor boundary.

Our thermodynamic analysis is consistent with the sedimentation model in that it indicates the H_2SO_4 droplets and vapor are thermodynamically stable in the lower cloud layer and below, respectively. Thermodynamic equilibrium may be further promoted by the autocatalytic behavior of H_2SO_4.[63] Industrially, H_2SO_4 is made by the reaction of H_2SO_4 with SO_3 to form pyrosulfate

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \qquad (7)$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 \qquad (8)$$

It is possible that an intermediate pyrosulfate on the H_2SO_4 droplets assists in maintaining equilibria in lower cloud deck boundary.

Thus, the assumption of a small oxygen gradient and equilibrium for $H_2O-SO_3-SO_2-O_2-H_2SO_4$ allows this model to reproduce some features of the lower atmosphere. Below about 40 km, H_2O and H_2SO_4 are predicted with reasonable accuracy. Other gases in the lower atmosphere may or may not be in equilibrium. Assuming CO comes from photon-assisted CO_2 decomposition (reaction 6), the lack of energetic photons in the lower atmosphere easily explains kinetic limitations on the formation of CO.

4. KINETIC ANALYSIS

As discussed, many of the atmospheric reactions are likely kinetically limited. Other investigators[35,47] have shown that only the lowest 10 km or so can be considered to be in complete

DOI: 10.1021/acsearthspacechem.7b00067
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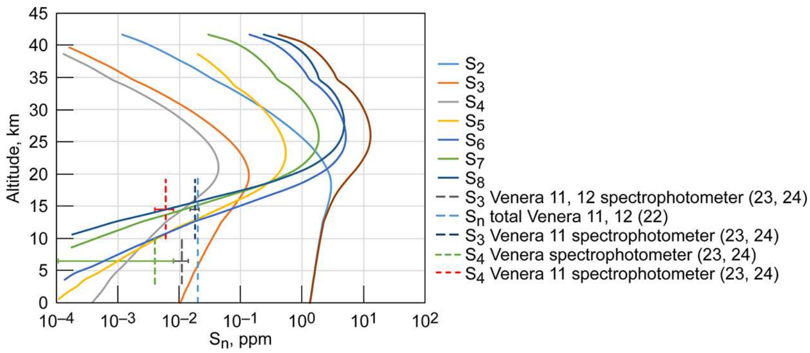

Figure 7. Calculations of elemental sulfur gas species compared to observations.

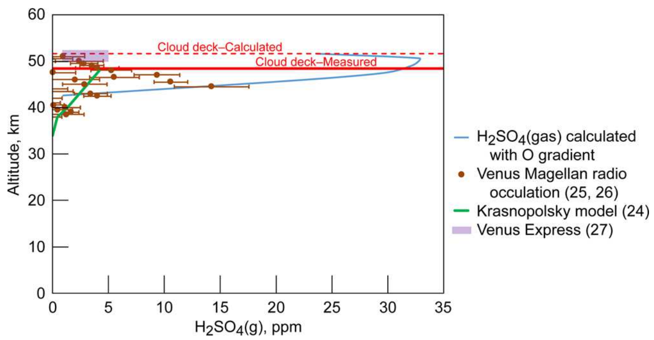

Figure 8. Calculated H_2SO_4 concentration compared to observations.

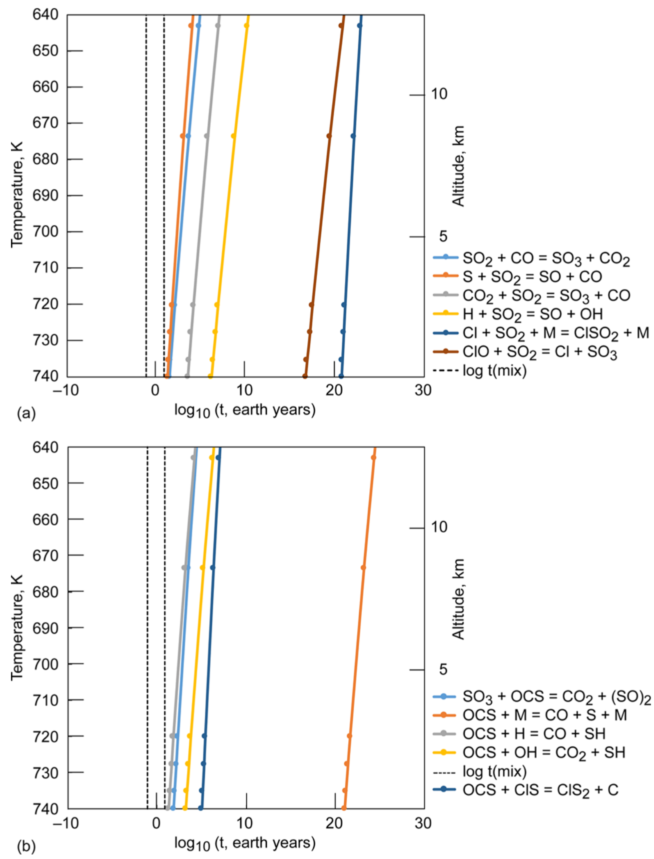

Figure 9. (a) Comparison of t_{mix} to t_{chem} for selected SO_2 consumption reactions. (b) Comparison of t_{mix} to t_{chem} for selected OCS consumption reactions.

thermodynamic equilibrium. Some key SO_2 consuming reactions are listed in Table 5. Using the methods described in the previous

Table 5. Kinetics of Some Key SO_2 Consuming Reactions[a]

reaction	rate	reference
$SO_2 + CO \rightarrow CO_2 + SO$	$(4.5 \times 10^{-12})e^{-24300/T}$	35
$SO_2 + S \rightarrow 2\ SO$	$(2.3 \times 10^{-11})e^{-5200/T}$	35
$SO_2 + H \rightarrow SO + OH$	$(3.7 \times 10^{-9}e)^{-14350/T}$	35
$SO_2 + CO_2 \rightarrow SO_3 + CO$	$(4.8 \times 10^{-12})e^{-35209/T}$[b]	35, 53
$SO_2 + Cl + M \rightarrow ClSO_2 + M$	$(1.3 \times 10^{-34})e^{-940/T}$	35, 51
$SO_2 + ClO \rightarrow Cl + SO_3$	4×10^{-18}	51

[a]Here T is absolute temperature in Kelvin. The units of the bimolecular rate constants are cm^3/sec and the units of termolecular rate constants are cm^6/sec. [b]Derived from the rate of the reverse reaction in ref 35 and the equilibrium constant calculated with the IVTAN code and database.[53]

section, chemical lifetime is compared to mixing lifetime. The rates are given in Table 5 and the comparison is shown in Figure 9a. None of the chemical lifetimes are equal to the mixing lifetimes. The SO_2 consumption kinetics indicate that few, if any, of the elementary reactions are expected to equilibrate in the Venusian atmosphere.

A similar situation exists for OCS consumption. Some key OCS consumption reactions are listed in Table 6. The rates are given in Table 6 and the comparison of chemical lifetime to mixing lifetime is shown in Figure 9b. Again, none of the chemical lifetimes are equal to the mixing lifetimes, indicating equilibration is not expected.

Table 6. Kinetics of Some Key OCS Consuming Reactions

reaction	rate	reference
$SO_3 + OCS \rightarrow CO_2 + (SO)_2$	$(1 \times 10^{-11})e^{-10000/T}$	35
$OCS + M \rightarrow CO + S + M$	$(2.2 \times 10^{-7})e^{-37300/T}$	35
$OCS + H \rightarrow CO + SH$	$(1.2 \times 10^{-11})e^{-1950/T}$	35
$OCS + OH \rightarrow CO_2 + SH$	$(1.1 \times 10^{-13})e^{-1200/T}$	35
$OCS + ClS \rightarrow ClS_2 + CO$	3×10^{-16}	51

Yet our calculations indicate some equilibration at elevations as high as 40 km, that is, the basic equilibrium matches observations in the lower atmosphere. Although we have rate expressions for many key elementary reactions,[35,51] these are generally measured under laboratory conditions (see, for example, ref 64) and would not include all the Venusian conditions. These conditions include catalysts such as metal chloride particles and/or self-catalysts and the high ambient pressures. It may be that some reactions actually have faster kinetics in the actual Venusian situation. This points to the need

DOI: 10.1021/acsearthspacechem.7b00067
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for continuing measurements and calculations of the rates of the elementary atmospheric reactions.

5. CONCLUSIONS

The lower 50 km of Venus from the surface to cloud deck is probably best described with a mixture of kinetic and thermochemical modeling. In this study, we examine the primary gas species and show that several features of the lower atmosphere can be described with thermochemical modeling using a free-energy minimizer. The vertical profile of the gases above the surface are modeled with the free energy minimizer by imposing a small oxygen gradient. This oxygen gradient is developed from the Vega 1 and 2 SO_2 vertical profile. It is within the experimental error of the nominal Venus gas composition and thus mass conservation is maintained. This gave good agreement for the H_2O and H_2SO_4 vertical profiles. It also allowed the approximate cloud deck altitude to be easily calculated. Equilibrium calculations for OCS, H_2S, and S_n (n = 1−8) show some agreement with data from the probes, suggesting that catalytic effects may also lead to near equilibrium for these species. However, the calculations for CO showed an increase near the surface instead of the observed decrease. The near agreement of some observations with equilibrium calculations is in apparent conflict with a kinetic analysis of some of the elementary reactions. This suggests the need for further measurements of reaction rates under conditions closer to those of the lower Venusian atmosphere. Catalysis either from particles in the atmosphere or self-catalysis in the case of H_2SO_4 forming reactions may also be important.

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Notes

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■ ACKNOWLEDGMENTS

Support from NASA Grant NNX14AN54G “Alteration of Basaltic Materials under simulated Venus Surface Conditions” is appreciated. B.F. was support by NSF Astronomy Program Grants AST-1412175 and AST-1517541.

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