

CHEMISTRY OF THE SURFACE AND LOWER ATMOSPHERE OF VENUS¹

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Abstract

We give a comprehensive review of the chemical interactions between the atmosphere and surface of Venus. Earth-based, Earth-orbital, and spacecraft data on the composition of the atmosphere and surface of Venus are presented and applied to quantitative discussions of the chemical interactions between carbon, hydrogen, sulfur, chlorine, fluorine, and nitrogen gases and plausible minerals on the surface of Venus. The results of our calculations are used to predict stable minerals and mineral assemblages on the surface of Venus, to determine which, if any, atmospheric gases are buffered by mineral assemblages on the surface, and to critically review and assess the prior work on atmosphere-surface chemistry on Venus. Several specific conclusions are presented. Some of these conclusions have been reached previously by other authors, while others are new to this work. These include the following: (1) The CO₂ pressure on Venus is identical within the uncertainties in the thermodynamic data to the CO₂ equilibrium partial pressure developed by the calcite + wollastonite + quartz assemblage at the mean Venus surface temperature of 740 K. However, the rate of this reaction under Venusian surface conditions is not known and needs to be measured experimentally to determine if this important reaction is capable of buffering CO₂ on Venus, (2) Chemical equilibrium calculations using the published thermodynamic data on scapolite minerals predict that meionite (CO₃²⁻-bearing scapolite) and sulfate meionite are unstable on the surface of Venus but that marialite (Cl-bearing scapolite) is stable on the surface, (3) The f_{O₂} of the Venusian lower atmosphere and surface is controlled by the CO/CO₂ ratio, and is too reducing for hematite to exist on the surface of Venus, as implied by spectral reflectance measurements made by Venera spacecraft. This apparent inconsistency may reflect kinetic inhibition of the hematite to magnetite conversion or the existence of a stable Fe³⁺-bearing mineral on the surface of Venus,

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Published in *Astronomicheskii Vestnik*, Vol. 26, No. 2, pp. 3-65, March-April, 1992. Original article submitted February 13, 1991.

(4) No pure hydrated silicates are thermodynamically stable on the Venusian surface with the possible exceptions of tremolite and phlogopite which may be stable at high altitudes. However, in any case, the formation of hydrated silicates apparently cannot explain the decreasing water vapor abundance near the surface of Venus. The least objectionable explanation is the formation of H_2CO_3 gas, (5) Atmospheric sulfur gases are not in chemical equilibrium with the Venusian surface. Laboratory reaction rate measurements show that SO_2 is the dominant sulfur gas on Venus because anhydrite formation, the thermodynamically favorable loss process, is too slow to reduce the SO_2 abundance down to the chemical equilibrium value, (6) The abundances of HCl and HF in the Venusian atmosphere are buffered by mineral assemblages on the Venusian surface, although the assemblages suggested previously in the literature are incorrect, and (7) No pure nitrogen-bearing minerals are thermodynamically stable on the Venusian surface although small amounts of nitrogen dissolved in silicates may constitute a significant fraction of the total nitrogen inventory on Venus.

1 Introduction

The global mean surface temperature on Venus is about 740 K and the global mean surface pressure is about 95 bars. Only a few percent of the solar flux incident on Venus manages to penetrate to the lower atmosphere below the clouds and the short wavelength solar UV radiation capable of photolyzing CO_2 , the dominant atmospheric gas, is stopped at high altitudes above the clouds. Venus would therefore appear to be a good natural laboratory for studying thermochemically driven atmosphere-surface reactions.

In this paper we present a detailed discussion of the chemistry of atmosphere-surface interactions on Venus. Rather than simply reviewing all the previous results, which are sometimes contradictory and often irrelevant because of new observational data, we will present illustrative calculations that update this previous body of work by incorporating the latest observational results and thermodynamic data. Furthermore we will then discuss where thermodynamic models of atmosphere-surface chemistry on Venus can be improved by laboratory measurements of new thermodynamic data or augmented by experimental studies of reaction rate kinetics. Finally we will conclude by summarizing the important issues facing us today about atmosphere-surface interactions on Venus and by suggesting theoretical, experimental, and observational studies which can improve our knowledge of these important questions.

2 Atmosphere-Surface Interactions on Venus

In the late 1950's, radio emission was detected from Venus and it was found that the brightness temperature of the thermal radio emission was 560 ± 73 K at 3.15 cm wavelength (Mayer *et al* 1958). These measurements provided the

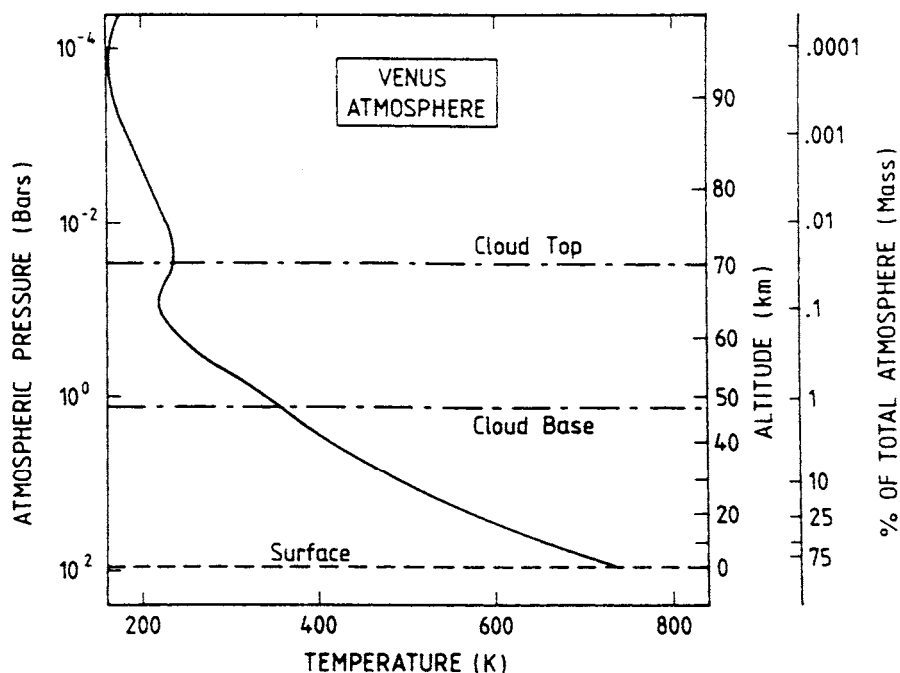


Figure 1. Pressure-temperature profile for the atmosphere of Venus in the 0 to 90 km altitude region. The 60° latitude model of Seiff (1983) was used to construct this plot.

first observational evidence for the high surface temperature of Venus, which was confirmed by the Mariner 2 encounter with Venus in December 1962 (Barath *et al* 1963, 1964). Shortly afterward, Mueller (1963) pointed out that the deduced surface temperature of ~ 700 K “corresponds with those attained during moderately high degrees of metamorphism on Earth. It is therefore possible that large parts of the atmosphere of Venus are partially equilibrated with the surface rocks. From this assumption, it follows that the composition of the atmosphere should reflect the mineralogical character of the rocks.”

Subsequent investigators adopted Mueller’s hypothesis of chemical equilibrium between the atmosphere and surface of Venus in order to explore the consequences for atmospheric chemistry and surface mineralogy. Mueller’s assumption is probably qualitatively correct for some (although not all) species. However it should also be noted that the Venus mean surface pressure of ~ 95 bars is significantly lower than the maximum pressure of ~ 15 kilobars reached in metamorphic reactions and that the H_2O partial pressure of ≤ 0.01 bars is significantly lower than H_2O pressures of several kilobars for many metamorphic reactions on Earth (e.g., see Vernon 1976). Both the lower total pressure and the lower water vapor partial pressure on Venus suggest that rates of gas-solid reactions at the surface of Venus will probably be more sluggish than the rates of analogous terrestrial metamorphic reactions, although the trace amounts of HCl and HF present in the atmosphere may increase reaction rates in some cases. Zolotov (1986b) has qualitatively discussed other similarities and differences between metamorphic and weathering reactions on the Earth and Venus.

Table 1. Composition of the Atmosphere of Venus*

Gas	Mixing Ratio	Altitude Range	References
CO ₂	0.965±0.008	≤ 100 km	Adams & Dunham 1932 von Zahn <i>et al.</i> 1983
H ₂ O	(1-40) ppm	cloud top	Bottema <i>et al.</i> 1964, 1965 Fink <i>et al.</i> 1972
	(20-200) ppm	below clouds	see text
HCl	0.6 ppm	cloud top	Connes <i>et al.</i> 1967
	0.4 ppm	cloud top	Young 1972
	0.4 ppm	cloud top	DeBergh <i>et al.</i> 1989
	0.5 ppm	42 km	Bézard <i>et al.</i> 1990
HF	5 ppb	cloud top	Connes <i>et al.</i> 1967
	10 ppb	cloud top	Young 1972
	4.5 ppb	42 km	Bézard <i>et al.</i> 1990
CO	45±10 ppm	cloud top	Connes <i>et al.</i> 1968
	51 ppm	cloud top	Young 1972
	(20-30) ppm	below clouds	Oyama <i>et al.</i> 1980 Gel'man <i>et al.</i> 1979
	45 ppm	42 km	Bézard <i>et al.</i> 1990
N ₂	0.035±0.008	≤ 45 km	von Zahn <i>et al.</i> 1983
	0.04±0.02	0-22 km	Hoffman <i>et al.</i> 1980a
	0.04±0.003	0-22 km	Istomin <i>et al.</i> 1979
	(0.034-0.046)	below clouds	Oyama <i>et al.</i> 1980
	0.025±0.003	22-42 km	Gel'man <i>et al.</i> 1979
SO ₂	(20-600) ppb	cloud top	Barker 1979 Conway <i>et al.</i> 1979 Stewart <i>et al.</i> 1979
	185±43 ppm	below clouds	Oyama <i>et al.</i> 1980
	130±35 ppm	below clouds	Gel'man <i>et al.</i> 1979
	(30-50) ppm	25-40 km	Berto <i>et al.</i> 1987
H ₂ S	3±2 ppm	<20 km	Hoffman <i>et al.</i> 1980a
S ₁₋₈	20 ppb	below clouds	Moroz <i>et al.</i> 1980 San'ko 1980
	(2-10) ppm	25-40 km	Berto <i>et al.</i> 1987
COS	0.3 ppm	below clouds	Bézard <i>et al.</i> 1990
SO	20±10 ppb	cloud top	Na <i>et al.</i> 1990
HDO	1.3±0.2 ppm	below clouds	DeBergh <i>et al.</i> 1991

*Excluding the noble gases.

Basic information about the composition of the atmosphere and surface of Venus is given in Tables 1 and 2, and the atmospheric (P,T) structure and the surface area distribution with altitude are illustrated in Figures 1 and 2. The atmospheric composition data in Table 1 is based on the comprehensive review by von Zahn *et al.* (1983); however, both references to the original discovery papers and to the more recent literature are given in the table. The information in these four figures and tables is referred to throughout this paper. We also note that, unless stated otherwise, we have relied on the JANAF Tables (Chase *et al.* 1985) and on the thermodynamic data compilations of Robie and colleagues (Robie *et al.* 1979; Hemingway *et al.* 1982) for the chemical equilibrium calculations presented here.

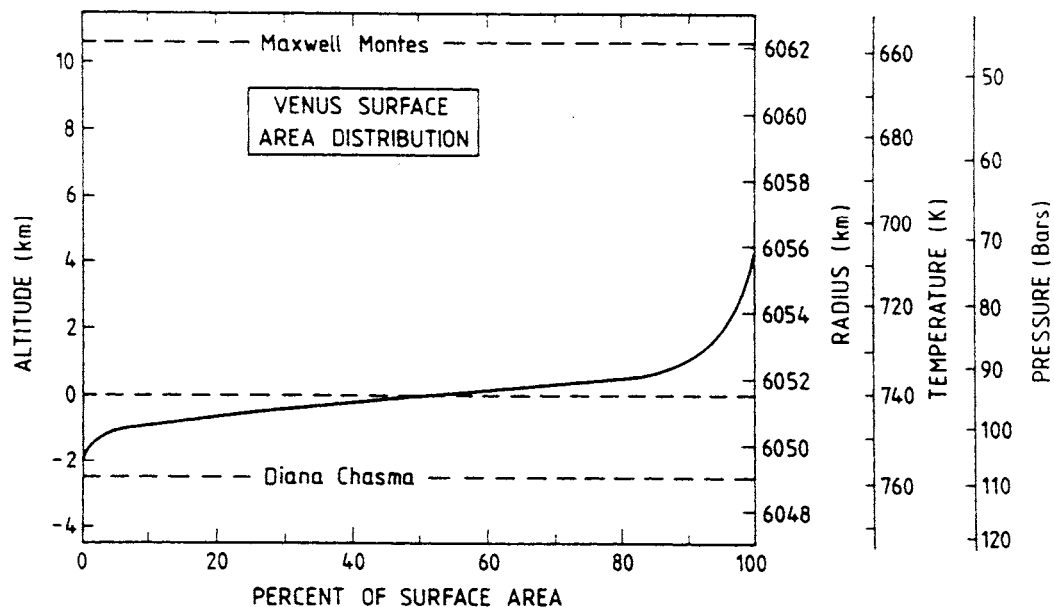


Figure 2. Surface area distribution on Venus as a function of altitude. The vertical scales indicate the altitude from the mean planetary radius of 6051.5 km, and the atmospheric temperature and pressure. The highest (Maxwell Montes) and lowest (Diana Chasma) points observed by Pioneer Venus are also shown. The Pioneer Venus radar altimetry data (Masursky *et al* 1980; Pettengill *et al* 1980), which cover 93% of the planet, and the 60° latitude (P,T) model of Seiff (1983) were used to construct this plot. Radar mapping of the entire planetary surface at higher resolution is likely to reveal points at both higher and lower altitudes than those found by Pioneer Venus.

2.1 Carbon Dioxide and Carbon Compounds

As Table 1 shows, CO₂ is the most abundant gas in the atmosphere of Venus and potentially it is also the most important gas that is reacting with the Venusian surface. Although the atmospheric abundance of CO₂ on Venus is well known there are no observations available of the elemental abundance of carbon in the Venus crust or of the presence and abundance of possible carbon-bearing phases such as carbonates, scapolites, etc. The Venera 13/14 and Vega 2 spacecraft which have analyzed the Venusian surface by X-ray fluorescence spectroscopy provided only elemental abundances for elements heavier than magnesium and were not able to detect carbon (see Table 2). However despite our lack of observational data about the mineralogical composition of the surface of Venus, theoretical models of atmosphere-surface interactions on Venus strongly suggest that carbonates are present on the surface and are responsible for regulating the CO₂ pressure in the atmosphere. But before discussing these models it is instructive to summarize current knowledge about the observed carbon inventories on Venus and the Earth.

Table 2. Composition of the Surface of Venus (Surkov *et al.*, 1984, 1986a)

Oxide	Chemical Composition (Mass % $\pm 1\sigma$)		
	Venera 13	Venera 14	Vega 2
MgO	11.4 \pm 6.2	8.1 \pm 3.3	11.5 \pm 3.7
Al ₂ O ₃	15.8 \pm 3.0	17.9 \pm 2.6	16 \pm 1.8
SiO ₂	45.1 \pm 3.0	48.7 \pm 3.6	45.6 \pm 3.2
K ₂ O	4.0 \pm 0.63	0.2 \pm 0.07	0.1 \pm 0.08
CaO	7.1 \pm 0.96	10.3 \pm 1.2	7.5 \pm 0.7
TiO ₂	1.59 \pm 0.45	1.25 \pm 0.41	0.2 \pm 0.1
MnO	0.2 \pm 0.1	0.16 \pm 0.08	0.14 \pm 0.12
FeO	9.3 \pm 2.2	8.8 \pm 1.8	7.7 \pm 1.1
SO ₃	1.62 \pm 1.0	0.88 \pm 0.77	4.7 \pm 1.5
Na ₂ O*	2.0 \pm 0.5	2.4 \pm 0.4	2.0
Total	98.1%	98.7%	95.4%

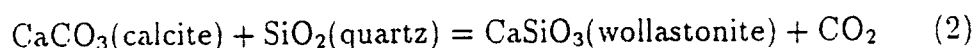
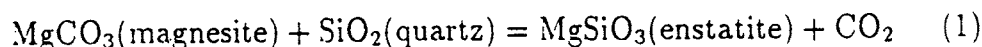
*Calculated by Surkov *et al.*

2.1.1 CO₂ Abundance on Venus and Earth

The Venusian surface pressure of 95 bars and the CO₂ volume mixing ratio of 0.965 ± 0.008 correspond to a CO₂ column density of 1.4×10^{27} molecules cm⁻². For comparison, the CO₂ mixing ratio in the terrestrial troposphere is ~ 340 ppm in nonurban regions and the corresponding column density is $\sim 4.8 \times 10^{21}$ molecules cm⁻² or about 290,000 times smaller than on Venus. However, according to Berner *et al.* (1983), the total amount of carbon present as carbonate, organic matter, etc. in the Earth's crust is equivalent to 7.4×10^{26} CO₂ molecules cm⁻² (or a global layer of calcite ~ 0.5 km thick). This crustal inventory is similar to the amount of CO₂ in the atmosphere of Venus, and if all this carbon were released into the Earth's atmosphere the CO₂ pressure would be ~ 53 bars instead of the current ~ 0.3 millibars. (This similarity was probably first noted by Wildt (1942) but both the CO₂ column density on Venus and the terrestrial crustal abundance of carbon accepted at that time have been superseded by better data). Thus the CO₂ which is chemically combined in crustal rocks on the Earth is instead found in the atmosphere on Venus because of the high surface temperature. How is this massive CO₂ atmosphere interacting with the surface of Venus today?

2.1.2 Carbonate-Silicate Equilibria and Atmospheric CO₂

Urey (1952, 1959) originally suggested that reactions such as



could control or buffer the CO₂ pressure in a planetary atmosphere. However the low surface temperature accepted at the time for Venus led Urey (1952) to dismiss reactions (1) and (2) as irrelevant to Venus because the equilibrium CO₂ pressures at low temperatures are much lower than the CO₂ pressure in

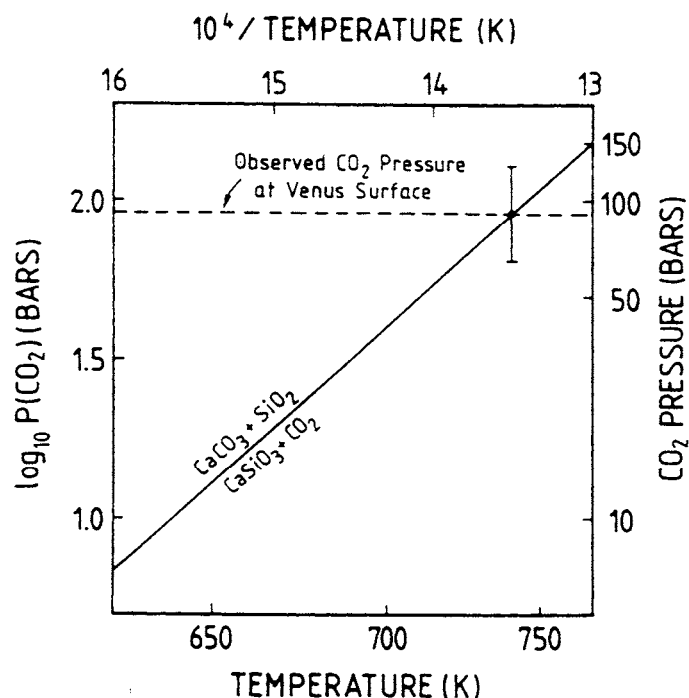


Figure 3. A comparison of the observed and predicted CO₂ pressures at the surface of Venus. The observed CO₂ mixing ratio in the atmosphere of Venus of $96.5 \pm 0.8\%$ and the total atmospheric pressure of 95.0 bars at the mean planetary radius of 6051.5 km yield a CO₂ pressure at the surface of 91.7 ± 0.8 bars. This is shown as the horizontal dashed line. The predicted CO₂ pressure from the Urey reaction ($\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$), which is a function of temperature, is calculated from thermodynamic data tabulated by Robie *et al* (1979) and Hemingway *et al* (1982). At the mean Venus surface temperature of ~ 740 K, the calculated CO₂ pressure from this reaction is 89^{+37}_{-26} bars. The observed and predicted CO₂ pressures intersect at the mean Venus surface temperature of ~ 740 K and are identical within the uncertainties ($\sim \pm 2.0$ kJ/mole) of the thermodynamic data.

the atmosphere of Venus. He concluded that "Venus owes its large nonequilibrium carbon dioxide atmosphere to the slowness of the chemical reactions and the lack of erosion, both the consequence of the absence of water."

After Mariner 2 confirmed Venus' high surface temperature, theorists began to reconsider carbonate-silicate equilibria as potential CO₂ buffers for the Venusian atmosphere because the equilibrium CO₂ pressures at high temperatures are comparable to that in the Venus atmosphere (e.g., Adamcik and Draper, 1963; Lewis 1968a, 1970a; Mueller 1963, 1964a; Vinogradov and Volkov, 1971). This is illustrated in Figure 3 where the equilibrium CO₂ pressure as a function of temperature for the wollastonite-calcite equilibrium [reaction (2)] is compared to the observed CO₂ pressure at the surface of Venus. The agreement between the observed CO₂ pressure of ~ 92 bars and the calculated CO₂ pressure of ~ 89 bars is striking and suggests that the wollastonite-calcite equilibrium is buffering the CO₂ pressure in Venus' atmosphere (e.g., Lewis, 1970a).

Because buffer reactions such as equations (1) and (2) have played a prominent role in chemical models of Venus during the past 3 decades we will briefly review the basic thermodynamic concepts involved in these models before proceeding further. The equilibrium constants for reactions (1) and (2) are given by the expressions:

$$K_1 = [a_{\text{MgSiO}_3} / (a_{\text{MgCO}_3} \cdot a_{\text{SiO}_2})] \cdot f_{\text{CO}_2} \quad (3)$$

$$K_2 = [a_{\text{CaSiO}_3} / (a_{\text{CaCO}_3} \cdot a_{\text{SiO}_2})] \cdot f_{\text{CO}_2} \quad (4)$$

where a_i is the thermodynamic activity of phase i and f_{CO_2} is the fugacity of CO_2 . A pure mineral has unit activity and a mineral which is a component in a solid solution has an activity which is proportional to its molar concentration in the solid solution. Unless stated otherwise, we assume that all the minerals involved in gas-solid reactions are pure phases and have unit activity. However, solid solutions are considered where it is appropriate to do so (e.g., olivine and pyroxene).

Likewise, the CO_2 fugacity is related to the CO_2 partial pressure P_{CO_2} via a multiplicative factor ϕ_i known as the fugacity coefficient. Fugacity coefficients are unity for ideal gases and may be either greater than or less than unity for real gases. They are useful because they allow us to model the thermochemical equilibria involving real gases, such as in the lower atmosphere of Venus by using tables of thermodynamic data for ideal gases (such as the JANAF Tables) combined with fugacity coefficients estimated from the principle of corresponding states (e.g., as described by Hirschfelder *et al* 1954).

For the case of CO_2 on Venus, the greatest deviations from ideality would be expected to occur at the highest temperatures and pressures near the surface. However, using the principle of corresponding states we can show that ideality is a good assumption for CO_2 on Venus because the surface temperature is about 2.5 times the CO_2 critical temperature (304 K) and the pressure is about 1.3 times the CO_2 critical pressure (72 bars). Under these conditions the estimated fugacity coefficient for CO_2 is unity to a good first approximation (e.g., see Lewis and Randall 1961).

We note that ideality is also a good assumption for all other gases in the Venusian atmosphere as long as the G.N. Lewis fugacity rule.

$$f_i(\text{mixture}) = y_i f_i(\text{pure}) \quad (5)$$

is valid. The G.N. Lewis fugacity rule relates the fugacity of a pure gas i to its fugacity in a gas mixture where gas i has a mixing ratio y_i . Equation (5) is a good approximation at low pressures where the gas phase is nearly ideal (Prausnitz *et al* 1986), as is the case for CO_2 on Venus. Thus the use of ideal gas chemical equilibrium calculations is justified and introduces significantly less uncertainty into our conclusions than does our imperfect knowledge of the atmospheric and surface composition.

Now, going back to equations (3) and (4), we see that since the thermodynamic activities of all minerals are assumed to be unity, the equilibrium constant is simply the CO_2 pressure. Solving for this as a function of tem-

perature by taking the appropriate thermodynamic data from Robie *et al* (1979) we obtain

$$\log_{10}P_{\text{CO}_2}(\text{magnesite}) = 8.62 - 4054(\pm 112)/T \quad (6)$$

$$\log_{10}P_{\text{CO}_2}(\text{calcite}) = 7.97 - 4456(\pm 98)/T. \quad (7)$$

Thus, at the Venusian surface temperature of ~ 740 K, the magnesite-enstatite equilibrium develops a CO_2 pressure of $\sim 1,400$ bars while the calcite-wollastonite equilibrium develops a CO_2 pressure of ~ 89 bars. Just what do these CO_2 pressures mean for the stability of magnesite and calcite on Venus?

Basically, the observed CO_2 pressure at the surface of Venus is sufficient for calcite + wollastonite + quartz to coexist but not for magnesite + enstatite + quartz to coexist. In other words, calcite + quartz will react to form wollastonite until either reactant is consumed or the equilibrium CO_2 pressure of 89 bars is generated, while magnesite + quartz will react to form enstatite until either reactant is consumed or the equilibrium CO_2 pressure of 1,400 bars is generated. Conversely, if the assemblage wollastonite + quartz + calcite is exposed to an external CO_2 pressure greater than the equilibrium pressure of 89 bars, wollastonite + CO_2 will react to form calcite + quartz until the CO_2 pressure is reduced to 89 bars or until all wollastonite is exhausted. Thus, the mineral assemblage wollastonite + quartz + calcite buffers the CO_2 pressure because variations in the CO_2 pressure (at constant temperature) are regulated by gas-solid reactions.

At this point it is natural to ask what conditions are required for the calcite-wollastonite equilibrium to take place on the Venusian surface. One of these conditions is that the different solid and volatile phases involved in the reaction are all present. Various authors have argued that calcite is absent on Venus because on the Earth it is formed by sedimentation from water. However, we note that calcite is also found in certain igneous rocks, such as carbonatites and nepheline-syenites (Deer *et al* 1963). As discussed later in section (2.4.3), the observed HCl abundance on Venus can be buffered by other mineral assemblages found in nepheline-syenites. Thus, an independent argument suggests that calcite-bearing igneous rocks are indeed present on Venus. Furthermore we also note that the high D/H ratio of $\sim 1.6\%$ on Venus (Donahue *et al* 1982) implies the existence of oceans and associated calcite formation via inorganic sedimentation, on Venus at some time in the past.

Another condition is that all the solid phases and the CO_2 be in chemical contact. Orville (1974) has interpreted this to mean that all the solid phases must be present in the same igneous rock. However, we note that the calcite + wollastonite + quartz assemblage could be formed from intimate mixing of different types of fine-grained materials produced by a combination of chemical and physical weathering processes acting on igneous rocks without the necessity for all minerals to have been present initially. For example, thermodynamic calculations by Khodakovsky *et al* (1979), which consider the chemical weathering reactions when several major rock types such as andesites, rhyolites, sodium alkaline basalts, and potassium alkaline basalts

are exposed to the Venusian atmosphere, predict that significant amounts of calcite will be formed from sodium and potassium alkaline basalts and that significant amounts of quartz will be formed from andesites and rhyolites. In this regard it is interesting to note that the Venera 8 gamma ray spectroscopic analyses for K, U, and Th, and the Venera 13 X-ray fluorescence data for major elements have been interpreted as a high-potassium alkaline basaltic composition (Volkov *et al* 1986). Another route for producing fine-grained calcite by a combination of chemical and physical weathering was proposed by Florensky *et al* (1977) and later quantified by Nozette and Lewis (1982). In this mechanism, which is discussed in more detail below, chemical weathering of rocks at high elevations produces calcite that is then abraded and blown into the hotter lowlands below. In turn, reaction of the calcite + quartz assemblage will yield wollastonite, as occurs in contact metamorphic rocks on the Earth. Thus, several thermodynamically feasible routes lead to the establishment of the calcite-wollastonite equilibrium.

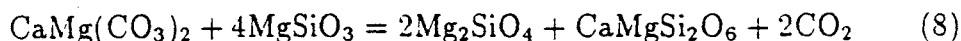
Another important question is the amount of calcite required for buffering the CO₂ pressure in the Venusian atmosphere. Unfortunately this information cannot be derived from equations (2) and (4) because the equilibrium constant for a buffering reaction does not depend on the *amount* of solid material present; as long as some is present the buffering can take place. However it is possible to make some mass balance calculations to illustrate how much calcite may be required. The total inventory of atmospheric CO₂ on Venus corresponds to a global calcite layer ~ 0.87 km thick, but the amount of calcite required for buffering is much smaller because only variations about the CO₂ equilibrium pressure of 89 bars for reaction (2) are involved. For example, if the surface CO₂ pressure were increased by ~ 0.02 bars, approximately 45 g cm^{-2} of calcite, equivalent to a layer ~ 17 cm thick would have to be formed to bring the CO₂ pressure back to that of the calcite-wollastonite equilibrium. Conversely, a 0.02 bar CO₂ pressure drop would consume the same amount of calcite, which would be equivalent to about 2 meters of Venusian surface material if all the CaO in the Venera and Vega analyses of the surface is present as calcite. Even though all the observed CaO probably is not present as calcite, Lewis (1971a) has noted that materials which are more calcium-rich than average Venus soil are probably responsible for the buffer so the amount of material required is probably less than 2 meters.

However, the apparent necessity to equilibrate ~ 20 to 200 cm of Venus surface material with the atmosphere in order to buffer even small CO₂ pressure variations raises the question of whether the rate of the calcite-wollastonite reaction is sufficiently rapid for equilibrium to be closely approached on a geologically short timescale. Several kinetic studies (e.g., Jander 1927; Repa 1954; Gordon 1971; Kridelbaugh 1973; Tanner *et al* 1985) have been done on reaction (2), but we cannot quantitatively estimate the rate of the calcite-wollastonite reaction on the Venusian surface because the required kinetic data have not been measured under the appropriate conditions.

For example, none of the studies measured the specific rate (molecules $\text{cm}^{-2} \text{sec}^{-1}$), which is required to calculate how fast CO_2 will react with exposed wollastonite on the Venusian surface. Also, the early kinetic studies are either done under conditions that allowed the formation of several other calcium silicates in addition to wollastonite (Jander 1927) or are only qualitative (Repa 1954). Kridelbaugh (1973) studied the rate of decarbonation of calcite + quartz powders in anhydrous CO_2 , but Tanner *et al* (1985) have pointed out that his data analysis and therefore his rate equation are incorrect. Thus his data *cannot* be used to constrain CO_2 production on Venus as Mueller and Kridelbaugh (1973) have attempted to do. Unfortunately the studies of Gordon (1971) and Tanner *et al* (1985) are probably also inappropriate to Venus because these workers used binary $\text{CO}_2 - \text{H}_2\text{O}$ gas mixtures containing 4% H_2O (Tanner *et al* 1985) or 82% H_2O (Gordon 1971), while the lower atmosphere of Venus contains only 20 – 200 ppm H_2O .

The work by Gordon (1971), Kridelbaugh (1973), and Tanner *et al* (1985) suggests that the mechanism of the decarbonation reaction of calcite + quartz is different under anhydrous and “wet” conditions and the kinetics are also probably different under anhydrous and “wet” conditions. It is not clear if the mechanism for the carbonation reaction of CO_2 + wollastonite is also different under anhydrous and “wet” conditions. However the careful study of Tanner *et al* (1985) shows that the rate limiting step for the carbonation reaction is quartz precipitation from a supercritical $\text{CO}_2 - \text{H}_2\text{O}$ fluid. If quartz precipitation remains rate limiting under Venusian surface conditions, the reaction rate is likely to be different than that measured by Tanner *et al* (1985) because of the different silica transport and precipitation mechanisms required in the absence of water.

Finally, it is interesting to ask if any other carbonates are likely to be thermodynamically stable on the surface of Venus. A detailed study by Lewis (1970a) of 19 different CO_2 buffer reactions involving carbonates shows that calcite is the only carbonate stable on the Venusian surface at 740 K. However, as Figure 4 illustrates, other carbonate-silicate mineral assemblages may also be stable on the Venusian surface but only at the lower temperatures found in the less extensive, higher elevation areas. For example, at equilibrium the reaction



between dolomite + enstatite yielding forsterite + diopside + CO_2 and the reaction



between magnesite + enstatite yielding forsterite + CO_2 , generate CO_2 pressures given by the equations

$$\log_{10} P_{\text{CO}_2}(\text{dolomite}) = 8.52 - 4511(\pm 286)/T \quad (10)$$

$$\log_{10} P_{\text{CO}_2}(\text{magnesite}) = 8.85 - 4903(\pm 120)/T \quad (11)$$

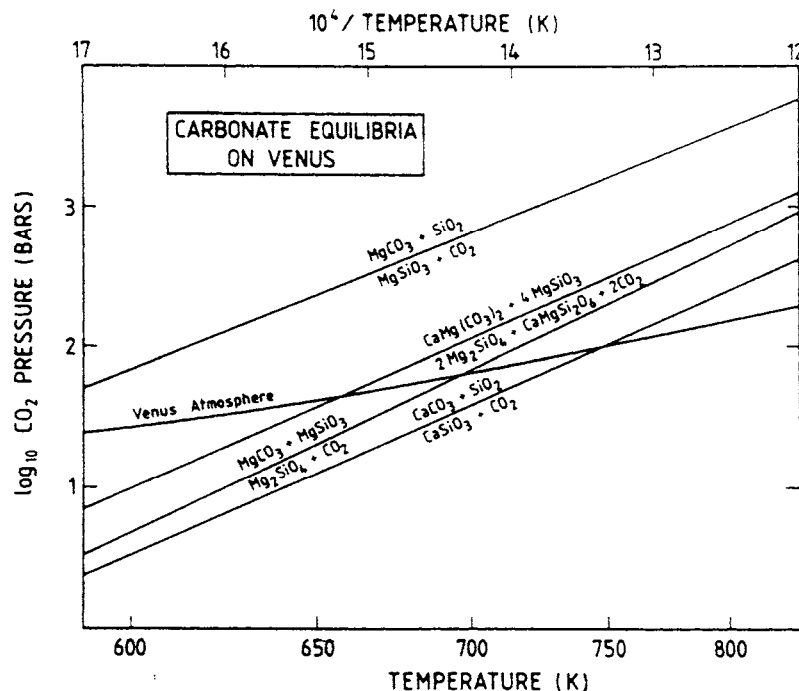


Figure 4. A comparison of the observed CO_2 pressure-temperature profile on Venus with the CO_2 pressures calculated for selected carbonate equilibrium reactions. The observed profile, which is adiabatic, is the 60° latitude model of Seiff (1983). Thermodynamic data from Robie *et al* (1979) and Hemingway *et al* (1982) are used to calculate the temperature dependent CO_2 pressures for selected carbonate equilibria taken from Lewis (1970a) and Nozette and Lewis (1982). For each reaction shown, silicates + CO_2 are stable below the log P vs. $1/T$ curve, carbonates + silicates are stable above the log P vs. $1/T$ curve, and all phases are stable along the curve. Thus, the assemblage $\text{MgSiO}_3 + \text{CO}_2$ is stable at all temperatures on the surface of Venus but the assemblage $\text{Mg}_2\text{SiO}_4 + \text{CO}_2$ is only stable in the hotter regions of the Venus surface and at higher elevations will begin to be converted to $\text{MgCO}_3 + \text{MgSiO}_3$ at ~ 700 K. Furthermore, if reaction rates are sufficiently rapid forsterite + CO_2 can be totally converted to magnesite + enstatite at lower temperatures which occur at even higher elevations. Likewise, if forsterite is in contact with diopside ($\text{CaMgSi}_2\text{O}_6$) on the Venus surface, this assemblage can react with the atmospheric CO_2 to form dolomite [$\text{CaMg}(\text{CO}_3)_2$] + enstatite at ~ 660 K. The predicted hypsometric control of mineral chemical weathering is discussed in more detail in the text.

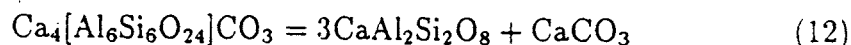
which intersect the CO_2 (P,T) profile in the Venusian atmosphere at temperatures of $\sim 660 \pm 70$ K ($P_{\text{CO}_2} \sim 48$ bars) and $\sim 700 \pm 30$ K ($P_{\text{CO}_2} \sim 70$ bars), respectively. The corresponding altitudes determined from the observed variation of temperature with altitude are ~ 10.5 km and ~ 5.3 km, respectively, above the median planetary radius of 6051.5 km.

Thus for reaction (8), the assemblage forsterite + diopside + CO_2 is stable at higher temperatures (lower elevations), the assemblage dolomite +

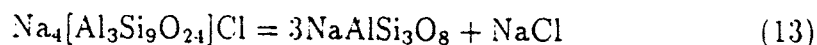
enstatite is stable at lower temperatures (higher elevations), and all phases coexist at ~ 660 K (~ 10.5 km altitude). Likewise for reaction (9), forsterite + CO_2 is stable at lower altitudes and magnesite + enstatite is stable at higher altitudes. This predicted hypsometric control of mineral stabilities, which was qualitatively discussed by Florensky *et al* (1977), has led Nozette and Lewis (1982) to suggest that "calcium- and magnesium-rich weathering products are produced at high altitudes by gas-solid reactions with igneous minerals, then removed into the hotter lowlands by surface winds. These fine-grained weathering products may then rereact with the lower atmosphere and buffer the composition of the observed gases carbon dioxide, water vapor, sulfur dioxide, and hydrogen fluoride in some regions of the surface. This process is a plausible mechanism for the establishment in the lowlands of a calcium-rich mineral assemblage, which had previously been found necessary for the buffering of these species."

2.1.3 Scapolite Minerals

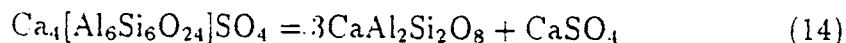
Another carbonate-bearing mineral which may be stable on the surface of Venus is scapolite, which is a three component solid solution commonly found in calcium-rich metamorphic rocks on the Earth (Deer *et al* 1963). The stabilities of the three end-members in the solid solution can be calculated from the decomposition reactions



for the decomposition of meionite to anorthite + calcite,



for the decomposition of marialite to albite + halite, and



for the decomposition of sulfate meionite to anorthite + anhydrite. Using the thermodynamic data tabulated by Moecher and Essene (1990) for meionite and sulfate meionite, and the data tabulated by Semenov *et al* (1981) for marialite, the equilibrium constants for reactions (12)–(14) are given by

$$\log_{10}K_{12} = 3.14 - 3468(\pm 569)/T \quad (15)$$

$$\log_{10}K_{13} = -2.40 + 3082(\pm 575)/T \quad (16)$$

$$\log_{10}K_{14} = 3.85 - 13976(\pm 612)/T. \quad (17)$$

These data show that both meionite and sulfate meionite are unstable relative to the assemblages anorthite + calcite and anorthite + anhydrite under all Venusian surface conditions. At 740 K, assuming that anorthite + calcite coexist, the calculated thermodynamic activity for meionite is ~ 0.03 with a range of ~ 0.005 – 0.2 being allowed by the uncertainty in the thermodynamic data. Similarly, assuming that anorthite + anhydrite coexist, the thermodynamic activity for sulfate meionite is $\sim 10^{-15}$ at 740 K. Thus, an isolated

grain of meionite on the surface of Venus will spontaneously decompose to a mixture of anorthite + calcite, and an isolated grain of sulfate meionite on the surface of Venus will spontaneously decompose to a mixture of anorthite + anhydrite. Neither mineral is stable as a pure phase nor is a binary solid solution of the two minerals stable under Venusian surface conditions.

In contrast, the thermodynamic data of Semenov *et al* (1981) for marialite show that it is stable on the Venusian surface relative to the assemblage albite + halite. Furthermore, the activity-composition relations for scapolite solid solutions (Moecher and Essene 1990) suggest that binary solid solutions of meionite + marialite will also be stable on the surface of Venus. Barsukov *et al* (1986) also concluded that meionite-marialite solid solutions are stable on Venus, but Volkov *et al* (1986) and Zolotov *et al* (1987) reached exactly the opposite conclusion that scapolites are *not* stable on Venus. However, none of these authors gave the source of their thermodynamic data and their work must therefore be viewed with caution.

Although the thermodynamic data of Semenov *et al* (1981) show marialite to be stable on Venus, we view this result with caution for several reasons. First, it is not clear if their data refer to marialite in which Al-Si and anions are totally ordered, totally disordered, or in an intermediate state. The degree of order/disorder affects the configurational entropy and hence the Gibbs free energy of formation for the scapolite sample. For example, Moecher and Essene (1990) show that contributions from Al-Si disorder and anion disorder may potentially comprise up to 12% of the total molar entropy of meionite at 298 K. The resulting uncertainty in ΔG_f° may be ~ 2 kJ/mole. It is impossible to estimate the importance of similar effects in the samples studied by Semenov *et al* (1981). Second, Orville (1975) concluded that marialite was unstable relative to albite + halite at 750°C and 4 kb. However, the Semenov *et al* data show that marialite is stable. Third, the Semenov *et al* data also seem to indicate a much greater stability for marialite than implied by terrestrial occurrences (Deer *et al* 1963). Thus, we believe that further thermodynamic studies of well characterized marialite samples are required prior to drawing firm conclusions about its stability on Venus.

2.1.4 The CO/CO₂ Ratio and the Oxygen Fugacity of the Lower Atmosphere

Carbon monoxide was discovered in the atmosphere of Venus by Connes *et al* (1968) who derived an abundance of 45 ± 10 ppm at the cloud tops. Young (1972) reanalyzed the Connes spectra and gave a revised CO abundance of 51 ± 1 ppm. Subsequent *in-situ* measurements by the Pioneer Venus and the Venera 11/12 gas chromatograph experiments of the CO abundance in the lower atmosphere of Venus gave mixing ratios of 32^{+62}_{-22} ppm at 52 km, 30 ± 18 ppm at 42 km, and 20 ± 3 ppm at 22 km (Oyama *et al* 1980) and 28 ± 7 ppm in the 36 to 42 km region and 17 ± 1 ppm at 12 km (Gel'man *et al* 1979; Marov *et al* 1989). More recent Earth-based spectroscopic observations at $2.3\mu\text{m}$ of the night side of Venus give a CO mixing ratio of 45 ppm in the 35 to 45 km altitude region (Bézar *et al* 1990). Within error, this value is the

same as that reported by Oyama *et al* (1980) for CO in the same altitude range.

Although CO is a trace constituent of the lower atmosphere of Venus it is nevertheless an important gas because the CO/CO₂ ratio in the hot, lower atmosphere controls the oxygen fugacity (f_{O_2}) of the atmosphere and probably also controls the oxidation state of the Venusian surface. This point is easily illustrated by considering the thermochemical equilibrium



which has an equilibrium constant K_{18} given by

$$K_{18} = (X_{CO_2}/X_{CO})^2 \cdot (1/f_{O_2}). \quad (19)$$

Taking thermodynamic data for the temperature dependent equilibrium constant K_{18} from the JANAF Tables (Chase *et al* 1985) and rearranging equation (19) we obtain

$$\log_{10} f_{O_2} = 2\log_{10}(X_{CO_2}/X_{CO}) + 9.20 - 29621(\pm 19)/T \quad (20)$$

which gives the f_{O_2} as a function of temperature (and thus altitude) and the CO/CO₂ ratio in the lower atmosphere of Venus. Inserting the CO/CO₂ ratio at 22 km then yields

$$\log_{10} f_{O_2} = 18.57 - 29621(\pm 19)/T \quad (21)$$

which we will assume is valid in the range of 0 to 22 km. We note that the Venera 11/12 gas chromatograph measured a CO mole fraction of 17 ± 1 ppm at 12 km altitude, but within the combined experimental uncertainties, this value is the same as the CO mole fraction of 20 ± 3 ppm measured by the Pioneer Venus gas chromatograph at 22 km.

The calculated oxygen fugacity as a function of temperature in the near surface region of Venus is shown in Figure 5 where it is seen that $f_{O_2} \sim 10^{-21.5}$ bars at ~ 740 K (the temperature at the mean planetary radius). However if the CO mixing ratio at the surface of Venus is actually lower than the value of 20 ppm prevailing at 22 km then the oxygen fugacity will be correspondingly higher. For example, CO mixing ratios of 10 ppm and 5 ppm would lead to oxygen fugacities of $\sim 10^{-20.9}$ bars and $\sim 10^{-20.3}$ bars, respectively. On the other hand, it is difficult to imagine ways to *reduce* the f_{O_2} below the value of $10^{-21.5}$ bars, which is appropriate for 20 ppm CO, unless we somewhat arbitrarily assume that the oxygen fugacity of the near-surface Venusian atmosphere is not fixed by the CO/CO₂ ratio (and thus not in equilibrium with the dominant atmospheric gas). This is an unlikely situation which we will not consider further.

Likewise, it is extremely difficult (if not impossible) to find plausible mechanisms to increase the calculated O_2 mixing ratio of $\sim 10^{-23.5}$ predicted at the Venusian surface by approximately 20 orders of magnitude in order to have agreement with the O_2 mixing ratios of 44 ± 25 ppm and 16 ± 7 ppm determined by the Pioneer Venus gas chromatography experiment at altitudes of 52 km and 42 km, respectively (Oyama *et al* 1980) or with

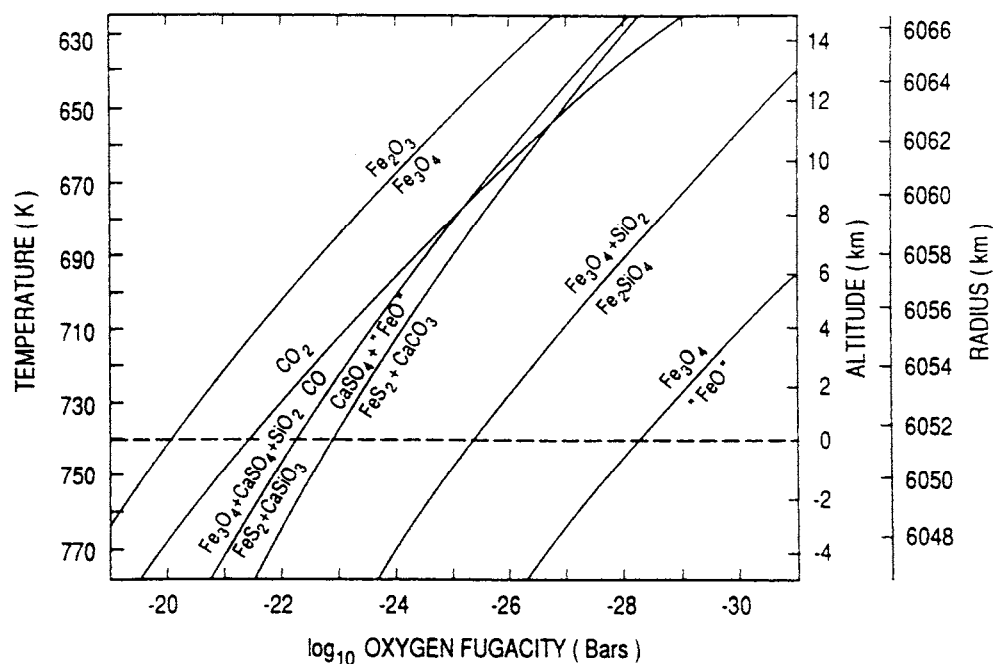


Figure 5. The temperature dependent oxygen fugacity (CO/CO_2) in the lower atmosphere of Venus is compared to the oxygen fugacities buffered by different iron-bearing mineral assemblages which may exist on the surface of Venus. Mineral assemblages to the right of the Venus atmosphere curve (CO/CO_2) are more reducing; those to the left are more oxidizing. As originally noted by Mueller (1964), the oxygen fugacity at the surface of Venus is inside the magnetite Fe_3O_4 stability field. Neither wüstite $\text{Fe}_{0.947}\text{O}$ nor hematite Fe_2O_3 is stable under equilibrium conditions on the Venus surface. The two curves involving pyrite FeS_2 are for oxygen fugacity buffers originally proposed by Mueller (1965) for the anhydrite + wollastonite buffer and by Lewis and Kreimendahl (1980) for the anhydrite + calcite buffer. Both reactions are discussed in more detail in connection with sulfide/sulfate equilibria on the surface of Venus.

the O_2 mixing ratio of 18 ± 4 ppm determined by the Venera 13/14 gas chromatography experiment in the 35 to 58 km altitude region (Mukhin *et al* 1983). However it is important to note that these measurements are also in conflict with the spectroscopic upper limit of $X_{\text{O}_2} < 0.3$ ppm at the cloud tops (Trauger and Lunine 1983), with the upper limit of $X_{\text{O}_2} < 20$ ppm anywhere below 42 km which was determined by the Venera 11/12 gas chromatography experiment (Gel'man *et al* 1979), and with the upper limit of $X_{\text{O}_2} < 50$ ppm anywhere below 60 km altitude which was determined by the Venera 11/12 spectrophotometer experiment (Moroz 1981).

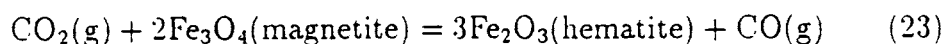
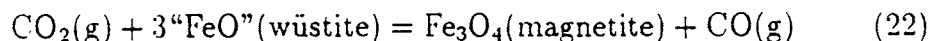
It is also important to realize that the large O_2 mixing ratios reported by the Pioneer Venus and Venera 13/14 gas chromatography experiments are incompatible with the observed sulfur chemistry of the atmosphere. As Craig *et al* (1983) have shown, the unobserved species SO_3 would be either the dominant or the second most abundant sulfur gas in the lower atmosphere

if these large O_2 mixing ratios are correct. In fact, as shown in Table 1, SO_2 is the dominant sulfur gas in the atmosphere of Venus.

Therefore for these reasons we will assume that the reported O_2 mixing ratios are in fact incorrect and will not use them as constraints on either the f_{O_2} of the Venusian atmosphere or the oxidation state of the Venusian surface in our subsequent discussion.

2.1.5 Constraints on the Oxidation State of the Venus Surface

Mueller (1963) was probably the first person to suggest that the CO/CO_2 ratio in the hot, lower atmosphere of Venus provided a constraint on the oxidation state and mineralogy of the surface of Venus. This constraint is due to gas-solid reactions exemplified by



which relate the Fe oxidation state in minerals on the Venusian surface to the oxidation state of the near-surface atmosphere. Despite the fact that CO had not yet been detected on Venus, Mueller (1964a) was able to use Kuiper's (1952) upper limit of $CO/CO_2 \leq 10^3$ to deduce that " $P_{O_2} \geq 10^{-27.1}$ atm at 700°K, which is in the center of the magnetite field."

This conclusion is still valid today and is graphically illustrated in Figure 5 where we see that the CO/CO_2 curve for f_{O_2} is inside the Fe_3O_4 stability field over all temperatures on the Venusian surface. The lower f_{O_2} end of the magnetite field is given by the equilibrium with "FeO"



which has an equilibrium oxygen fugacity given by

$$\log_{10}f_{O_2} = 13.055 - 30635(\pm 690)/T \quad (25)$$

valid from 600 to 800 K (Robie *et al* 1979). The upper f_{O_2} end of the magnetite field is given by the equilibrium with Fe_2O_3



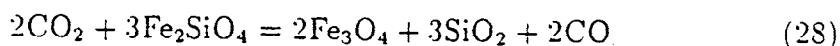
with an equilibrium oxygen fugacity given by

$$\log_{10}f_{O_2} = 14.71 - 25790(\pm 600)/T \quad (27)$$

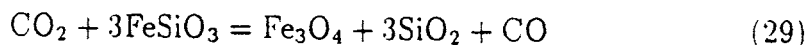
valid over the same temperature range (Robie *et al* 1979). Thus, magnetite is predicted to be stable on the Venusian surface while "FeO" (wüstite) is predicted to be absent from the Venusian surface because oxygen fugacities which are ~ 7 orders of magnitude more reducing than CO/CO_2 are needed for wüstite to be stable. Likewise, Fe_2O_3 (hematite) is also predicted to be absent from the surface of Venus because it requires f_{O_2} values about 25 times more oxidizing than CO/CO_2 in order to be stable.

Despite this fact, Zolotov (1987) has predicted that Fe_2O_3 will be stable in the Venus highlands at ~ 3 km altitude. But this assertion is based on the assumption that the gas phase equilibrium (18) between CO and CO_2 will be quenched at the 740 K value, while the gas-solid reaction (26) between Fe_3O_4 and Fe_2O_3 will continue to reach equilibrium. This is an unlikely situation because gas phase reactions are generally more rapid than gas-solid reactions. Furthermore, the Fe_3O_4 - Fe_2O_3 reaction (26) is noted for being sluggish and slow to attain equilibrium (e.g., see O'Neill 1988; Hemingway 1990). Of course, as discussed in more detail below, the rate of the magnetite \rightarrow hematite conversion and the reverse reaction should be measured under conditions appropriate to the surface of Venus in order to quantitatively assess Zolotov's suggestion. But at the present time we believe that there is very little evidence in favor of the magnetite \rightarrow hematite conversion being a facile reaction and we will base the rest of our discussion on the result shown in Figure 5 that magnetite is the stable Fe oxide over the entire surface of Venus.

However as Mueller and subsequent investigators have realized (e.g., Lewis 1970a, 1971b; Lewis and Kreimendahl 1980; Mueller 1964a, 1965; Zolotov 1986a), Fe oxides are probably not the only Fe-bearing minerals present on the surface of Venus and it is also interesting to consider the stabilities of FeO-bearing silicates such as olivine $(\text{Mg, Fe})_2\text{SiO}_4$ and low-Ca pyroxene $(\text{Mg, Fe})\text{SiO}_3$. These minerals can interact with the CO_2 and CO in the Venusian atmosphere via reactions exemplified by



between CO_2 + fayalite yielding magnetite + quartz + CO and by



between CO_2 + ferrosilite yielding magnetite + quartz + CO.

Actually neither pure fayalite nor pure ferrosilite is expected on the Venus surface. Ferrosilite FeSiO_3 does not occur in nature and as Figure 5 illustrates, the calculated f_{O_2} at the Venusian surface is ~ 4 orders of magnitude too oxidizing for pure fayalite Fe_2SiO_4 to be thermodynamically stable against oxidation to magnetite + quartz. Instead both fayalite and ferrosilite are probably present dissolved in olivine and low-Ca pyroxene solid solutions formed with the magnesium endmembers Mg_2SiO_4 and MgSiO_3 . But how much Fe_2SiO_4 or FeSiO_3 can be dissolved in olivine or low-Ca pyroxene under Venusian surface conditions?

We can answer this question by first using the equilibrium constants for reactions (28) and (29) to calculate the activities of fayalite and ferrosilite in the two solid solutions and then using activity-composition models to calculate the compositions of the olivines and pyroxenes. Taking thermodynamic data from Robie *et al* (1979) and Helgeson *et al* (1978) we calculate that

$$\log_{10} a_{\text{Fa}} = \frac{2}{3} \log_{10} (X_{\text{CO}}/X_{\text{CO}_2}) + 0.364 + 1060(\pm 160)/T \quad (30)$$

Table 3. Predicted Composition of Olivine and Pyroxene on the Venus Surface

Altitude (km)	Temperature (K)	$\log_{10} f_{O_2}$ (bars)	Olivine Mole % Fa and Range	Pyroxene Mole % Fs and Range
-4	770	-19.9	10.8 (8.4 - 13.9)	20.8 (13.4 - 32.1)
-2	755	-20.7	11.0 (8.5 - 14.3)	21.4 (13.7 - 33.4)
0	740	-21.5	11.2 (8.6 - 14.6)	22.1 (14.0 - 34.7)
2	725	-22.3	11.5 (8.8 - 15.0)	22.8 (14.4 - 36.2)
4	710	-23.2	11.7 (9.0 - 15.5)	23.6 (14.7 - 37.8)
6	695	-24.1	12.0 (9.1 - 16.0)	24.4 (15.1 - 39.5)
8	679	-25.1	12.3 (9.3 - 16.6)	25.4 (15.5 - 41.5)
10	663	-26.1	12.7 (9.5 - 17.2)	26.4 (15.9 - 43.8)
12	648	-27.1	13.0 (9.6 - 17.8)	27.5 (16.4 - 46.1)

$$\log_{10} a_{Fs} = \frac{1}{3} \log_{10} (X_{Co}/X_{Co_2}) + 0.235 + 496(\pm 146)/T \quad (31)$$

where a_{Fa} and a_{Fs} are the thermochemical activities of fayalite in olivine and ferrosilite in low-Ca pyroxene. Again, assuming a constant CO mixing ratio of 20 ppm we derive

$$\log_{10} a_{Fa} = -2.76 + 1060(\pm 160)/T \quad (32)$$

$$\log_{10} a_{Fs} = -1.326 + 496(\pm 146)/T \quad (33)$$

for Venusian surface conditions. Low-Ca pyroxene shows nearly an ideal one-site solid solution between Fe and Mg (Kern and Weisbrod 1967) so we may use the a_{Fs} from equation (33) as the ferrosilite mole fraction X_{Fs} in low-Ca pyroxene.

However, olivine is not an ideal Fe-Mg solid solution at Venusian surface temperatures. Instead it is nonideal and is represented as a sub-regular two site solid solution using an equation modified from Wood (1987)

$$\log_{10} a_{Fa} = \log_{10} X_{Fa}^2 + (1 - X_{Fa})^2 (1 + 2X_{Fa}) \cdot 2318/T. \quad (34)$$

The fayalite mole fraction X_{Fa} in olivine is then calculated by solving equations (30) and (34) simultaneously. Table 3 shows the predicted compositions of olivine and low-Ca pyroxene (along with the range of values due to the uncertainties in the thermodynamic data) as a function of altitude.

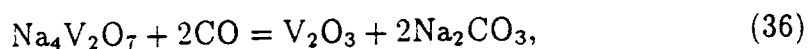
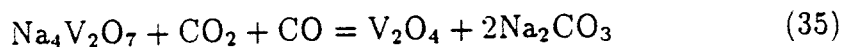
The results of the thermodynamic calculations show that under equilibrium conditions more Fe_2SiO_4 dissolves in olivine and more $FeSiO_3$ dissolves in low-Ca pyroxene in rocks in the highland regions than in the lowland regions of Venus. In other words, the "FeO" content of olivine and low-Ca pyroxene increases with increasing altitude (and thus with decreasing temperature) on Venus. At ~ 740 K (in the lowlands), olivine containing up to ~ 9 -15 mole % Fe_2SiO_4 (Fa_{9-15}) and low-Ca pyroxene containing up to ~ 14 -35 mole % $FeSiO_3$ (Fs_{14-35}) are predicted to be stable while more "FeO"-rich olivine and low-Ca pyroxene will be oxidized via reactions such as equations (28) and (29). However at ~ 10 km altitude (e.g., on Maxwell Montes) where

the temperature is ~ 663 K, more "FeO"-rich olivine (Fa_{13-17}) and low-Ca pyroxene (Fs_{16-44}) are stable. For comparison we note that Zolotov (1987) predicted that olivine with ≤ 10 mole % Fe_2SiO_4 and pyroxene with ≤ 30 mole % FeSiO_3 would be resistant to oxidation at ~ 735 K. However he did not present any results for other temperatures.

The thermodynamic predictions can also be compared to the (limited) observational data about the oxidation state of the Venusian surface. Pieters *et al* (1986) used a combination of the Venera 9/10 wide angle photometer measurements and the Venera 13/14 color images to derive the spectral reflectance of the Venusian surface in the $0.54\mu\text{m} - 1.0\mu\text{m}$ range. They found that at visible wavelengths the spectral reflectance of the Venusian surface was not diagnostic about the Fe oxidation state (with either Fe^{2+} - or Fe^{3+} -bearing minerals being acceptable), but that a high reflectance in the near IR region apparently required Fe^{3+} -bearing phases. However, as Pieters *et al* (1986) noted and as Figure 5 graphically illustrates, the presence of Fe^{3+} -bearing minerals such as hematite is not consistent with thermodynamic equilibrium predictions about the oxidation state of the Venusian surface. How can the apparent discrepancy between the conclusions of Pieters *et al* (1986) and the thermodynamic equilibrium predictions be explained?

Obvious explanations such as instrumental artifacts and the presence of minor phases with just the right spectral reflectance properties have been discussed by Pieters *et al* (1986) who point out that such explanations are unlikely although they cannot be totally rejected. They then suggested that the two most plausible explanations left are either the existence of a more oxidizing environment at the Venusian surface or incomplete equilibrium between the surface mineralogy and the (more reduced) lower atmosphere.

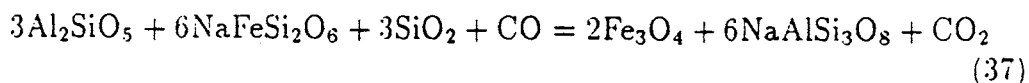
From our previous discussion in section (2.1.4) we see that the postulated existence of a more oxidizing environment near the surface of Venus would require a lower CO mixing ratio near the surface than is actually observed in the 12 - 22 km altitude region. In fact, the CO mixing ratio must be decreased to ~ 4 ppm in order to reach the Fe_3O_4 - Fe_2O_3 boundary. Higher oxygen fugacities would require even lower CO mixing ratios. However, extrapolating the apparent trend in the Pioneer Venus and Venera 11/12 data for CO downward to the Venusian surface gives a CO mixing ratio of ~ 13 ppm, corresponding to $f_{\text{O}_2} \sim 10^{-21.2}$, which is an order of magnitude too oxidizing for hematite. We also note that the "Contrast" experiment on Venera 13/14, which qualitatively measured the f_{O_2} from the color change taking place on an indicator plate as a result of the reactions



indicated $f_{\text{O}_2} \leq 10^{-21}$ (Florensky *et al* 1983; Volkov *et al* 1986), which is inside the magnetite field. Thus, f_{O_2} values $\geq 10^{-20.1}$, which are appropriate for the magnetite-hematite boundary at ~ 740 K, appear unlikely but cannot be definitively ruled out until either the CO mixing ratio or the oxygen fugacity has been measured quantitatively in the 0 - 12 km altitude range on Venus.

The second possibility that the surface mineralogy may be incompletely equilibrated with the Venusian atmosphere is certainly plausible but it is impossible to evaluate quantitatively because the required reaction rate measurements have not yet been made. As noted earlier, reaction (26) which converts Fe_3O_4 and Fe_2O_3 is slow at temperatures below 1000 K (e.g., see O'Neill 1988; Hemingway 1990), but the kinetics of this reaction have not been measured under Venusian surface conditions. Likewise no kinetic data are available for oxidation – reduction reactions between other Fe^{3+} - and Fe^{2+} -bearing minerals. Thus it is currently impossible to estimate the timescales for the reduction of any primary Fe^{3+} -bearing minerals which may have been brought to the surface of Venus in basaltic magma.

A third possibility, which was not considered by Pieters *et al* (1986), is that a stable Fe^{3+} -bearing mineral may be produced on the Venusian surface as the result of chemical weathering reactions. We studied this alternative quantitatively for three ferric minerals for which thermodynamic data are available. Acmite [ideally $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$], is a Fe^{3+} -bearing pyroxene commonly found in alkaline rocks on the Earth (Deer *et al* 1963). Acmite stability on the Venusian surface is controlled by redox reactions exemplified by



which has the equilibrium constant

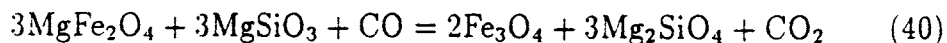
$$\log_{10}K_{37} = 13.92 + 4321(\pm 1506)/T \quad (38)$$

from 600 to 800 K. Thermodynamic data from Bennington and Brown (1982) for acmite and from Robie *et al* (1979) for other phases were used to calculate this equation. Taking 20 ppm CO, equation (38) shows that acmite is unstable under Venusian surface conditions; at equilibrium the acmite thermodynamic activity is $\sim 3 \times 10^{-3}$, which is far too low to be important even as the component of a pyroxene solid solution.

Magnesioferrite MgFe_2O_4 is a spinel group mineral which on the Earth is found with Fe^{2+} partially substituting for Mg^{2+} (Deer *et al* 1963). Magnesioferrite stability on the surface of Venus is controlled by redox reactions exemplified by



in felsic rocks and exemplified by



in mafic rocks. The equilibrium constants calculated using data from Robie *et al* (1979) are

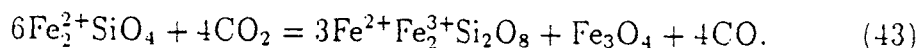
$$\log_{10}K_{39} = 0.91 + 7225(\pm 451)/T \quad (41)$$

$$\log_{10}K_{40} = 1.61 + 4678(\pm 467)/T \quad (42)$$

and the corresponding thermodynamic activities for magnesioferrite are ~ 0.01 in felsic rocks and ~ 0.08 in mafic rocks. Thus, magnesioferrite is unstable as a pure phase; however, it may be present as a minor component dissolved in magnetite. But it is unlikely that a magnetite-rich magnesioferrite solid solution would give the spectral signature observed by Pieters *et al* (1986).

Finally, Nikolayeva (1989) suggested that chemical weathering reactions could produce epidote [ideally $\text{Ca}_2\text{Fe}^{3+}\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})$], which terrestrially is produced during retrograde metamorphism (Deer *et al* 1963). However we show later in our discussion of hydrated silicates that epidote is thermodynamically unstable on Venus because the water vapor content of the atmosphere is so small.

Thus, none of the common ferric minerals for which thermodynamic data are available appear capable of explaining the observations of Pieters *et al* (1986). No thermodynamic data is available to assess the stabilities of other common ferric minerals such as Fe^{3+} -bearing phlogopite and amphiboles. However, the most interesting candidate mineral is laihunite (ideally $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{Si}_2\text{O}_8$) which is a nonstoichiometric distorted olivine-type mineral found in nature and also produced by the oxidation in air of synthetic fayalite (Kitamura *et al* 1984; Kondoh *et al* 1985). Laihunite could be produced during olivine oxidation on Venus via reactions exemplified by



Olivine oxidation has been studied by several investigators (e.g., Champness 1970; Haggerty and Baker 1967; Wu and Kohlstedt 1988, and references therein). However all these studies have been done in air and no information is available on the analogous reaction in CO/CO_2 gas mixtures.

2.2 Water and Hydrogen Compounds

2.2.1 The Abundance of Atmospheric Water Vapor

The atmosphere of Venus is extremely dry. Earth-based spectroscopic observations from ground-based telescopes (e.g., Barker 1975) and from high flying aircraft (Fink *et al* 1972; Kuiper *et al* 1969) show that the atmosphere above the clouds contains $\sim 1 - 40$ ppm water vapor and that the amounts are variable. A variety of *in situ* spacecraft measurements (e.g., see the reviews by von Zahn *et al* 1983 and Krasnopolsky 1986) and recent Earth-based spectroscopic observations (Bézard *et al* 1990) show that the atmosphere below the clouds contains $\sim 20 - 200$ ppm water vapor and that the amount is variable with altitude. For comparison, the terrestrial troposphere contains $\sim 1 - 4\%$ water vapor.

It is difficult to measure the small amounts of water vapor present in the atmosphere of Venus. Ground-based spectroscopic observations have to contend with interference from the telluric water lines which are stronger than the water lines in the atmosphere of Venus. *In situ* spacecraft experiments, such as mass spectrometers, have to avoid (or be corrected for) contamination from residual terrestrial water in the instrument. Other spacecraft

experiments, such as gas chromatographs and water vapor detectors based on conductivity measurements, have to avoid contamination by the strong acids (e.g., HF, HCl, and H₂SO₄) in the Venusian atmosphere. In fact, many of the early ground-based spectroscopic observations and many of the *in situ* measurements were affected by such problems and incorrectly indicated higher water vapor abundances than are actually present on Venus.

For example, water vapor detectors using chemical absorbents such as P₂O₅, LiCl, and CaCl₂ were flown on several Venera spacecraft and on the Vega 1/2 spacecraft (Vinogradov *et al* 1971; Surkov *et al* 1983, 1986b). However, these devices are susceptible to errors because of the presence of strong electrolytes such as HF, HCl, and H₂SO₄ on Venus and generally indicated significantly higher H₂O contents than implied by Earth-based microwave observations of sub-cloud water vapor (e.g., Janssen and Klein 1981) or than measured by other instruments on the same spacecraft. Likewise, the Pioneer Venus (PV) gas chromatography experiment (Oyama *et al* 1980) reported significantly higher H₂O contents (of 5200 ppm at 42 km and 1350 ppm at 22 km) than either the PV mass spectrometer (see Fig. 8 in Hunten *et al* 1989; Hoffman *et al* 1980b) or the scanning spectrophotometer experiment on the Venera 11/12 and Venera 13/14 spacecraft (Moroz 1983; Moroz *et al* 1979, 1983).

These apparent discrepancies have led to much debate and theorizing about the water vapor content of the Venusian atmosphere below the clouds. For example, Grinspoon (1987) and Grinspoon and Lewis (1988) take the global mean water vapor abundance on Venus as 20 ppm, Lewis and Grinspoon (1990) estimate a slightly higher global mean abundance of 50 ± 20 ppm, and Donahue in Hunten (1989) suggests that the global mean water vapor abundance is probably 200 ± 100 ppm. Furthermore data from the net flux radiometers on the 3 Pioneer Venus small probes suggest that below the clouds, the water vapor abundance is spatially variable with mixing ratios of 20–50 ppm near 60° N latitude, 200–500 ppm near 30° S latitude, and >500 ppm near the equator (Revercomb *et al* 1985).

However several recent developments have probably resolved this issue in favor of the lower water vapor contents determined by optical spectroscopy and mass spectroscopy. The first development is that an independent analysis of the Venera 11/12 scanning spectrophotometer data by Young *et al* (1984) confirms the conclusions of Moroz *et al* (1979) that the water vapor content below the clouds is ≤ 200 ppm and decreases to a value of ~ 20 ppm near the surface of Venus. The second development is that the scanning spectrophotometer experiment on the Venera 13/14 spacecraft also confirms the results of the earlier measurements made on the Venera 11/12 spacecraft (Moroz 1983; results of Moroz *et al* reviewed in Krasnopolsky 1986). The third development is that Donahue has been able to deconvolve the contributions of terrestrial and Venusian water to peaks in the PV mass spectrometer by virtue of the dramatically different D/H ratios for water on the two planets. This deconvolution leads to a water vapor profile similar to that determined by Moroz and his colleagues. Finally, recent Earth-based spectroscopic ob-

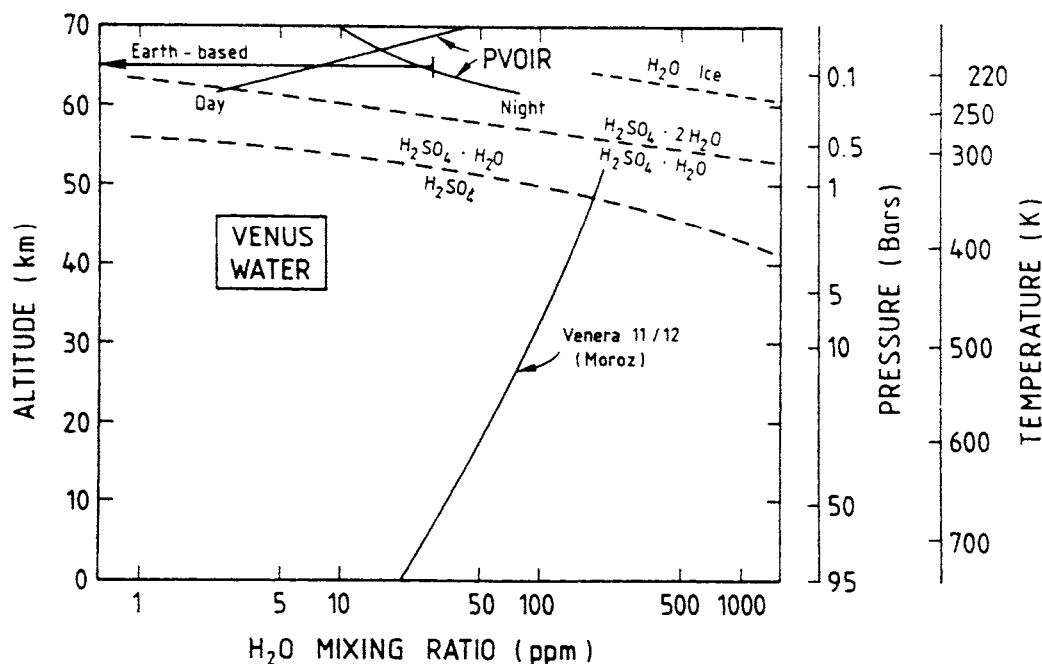
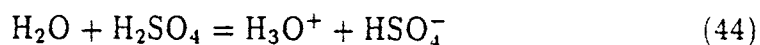


Figure 6. The vertical distribution of water vapor in the atmosphere of Venus. The three different sets of measurements shown are (1) Earth-based spectroscopic data (Barker 1975; Fink *et al* 1972; Kuiper *et al* 1969), (2) Pioneer Venus Orbiting Infrared Radiometer (PVOIR) data (Schofield *et al* 1982), and (3) scanning spectrophotometer data from Venera spacecraft (Moroz 1983; Moroz *et al* 1979, 1983). Dotted lines showing the water vapor pressures over water ice and over concentrated sulfuric acid solutions (calculated from JANAF data) are also shown. As originally noted by Young (1973), the decreasing water vapor concentration near the cloud tops (60–70 km) is consistent with the low water vapor pressures over concentrated sulfuric acid solutions. However, the dropoff in water vapor in the lower atmosphere of Venus is still unexplained although several possible mechanisms have been suggested.

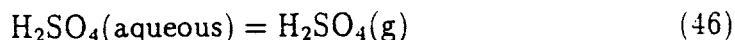
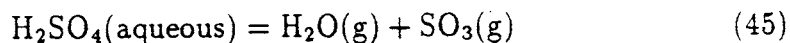
servations at $2.3\mu\text{m}$ of the night side of Venus give a H_2O mixing ratio of 40 ppm in the 35 to 45 km altitude-region (Bézar *et al* 1990).

Taken together these results suggest that the water vapor content of the lower Venusian atmosphere is ~ 200 ppm at ~ 52 km and decreases to ~ 20 ppm near the surface. However this water vapor profile is difficult to explain. As shown in Figure 6, the water vapor profile on Venus apparently reaches a maximum at ~ 50 to 60 km and decreases at higher and lower altitudes. The decrease at higher altitudes is consistent with the decreasing water vapor pressure over the concentrated sulfuric acid droplets that make up the clouds of Venus (e.g., see Young 1973). Concentrated sulfuric acid is a powerful dessicating agent because of reactions exemplified by



which lead to very low concentrations of unbound H_2O in concentrated sulfuric acid solutions and thus to very low water vapor pressures over these solutions. Thermodynamic data [e.g., from the JANAF Tables (Chase *et al*

1985] shows that the resulting water vapor pressures over aqueous sulfuric acid solutions containing 73–84 mass % H_2SO_4 , which make up the clouds of Venus (Young 1973; Hansen and Hovenier 1974; Esposito *et al* 1983), are low enough to explain the observed water vapor mixing ratios at the cloud tops of Venus. However, this mechanism cannot also explain the decreasing water vapor abundances in the lower atmosphere of Venus because the sulfuric acid solutions evaporate via reactions exemplified by



at the cloud base (~ 48 km) and are not present below this level.

We note that the vertical and meridional distribution and the temporal variation of water vapor in the lower atmosphere of Venus can be probed using the newly discovered infrared windows at $2.3\mu\text{m}$, $1.7\mu\text{m}$, and shorter wavelengths (e.g., Kamb *et al* 1988; Crisp *et al* 1989; Bézard *et al* 1990). Thus, we anticipate that in the near future, Earth-based and Galileo NIMS observations will greatly increase our knowledge of the abundance, distribution, and variability of water vapor in the lower atmosphere of Venus. However, we are still left with a question about the cause of the observed decrease in water vapor at lower altitudes.

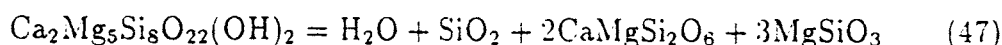
2.2.2 Hydrated Silicates

One possibility is the presence of hydrated minerals on the surface of Venus. If these were stable on the Venusian surface they could provide a sink for atmospheric H_2O by reaction of anhydrous silicates with water vapor to form hydrated silicates. In addition, the presence of hydrated minerals would have important consequences for the geochemistry, geology, and geophysics of the interior of Venus. Small amounts of water markedly decrease the melting point of rocks, with as little as 0.5% (by mass) decreasing the melting point by 200° . In addition to decreasing the melting point, water also affects the composition of the melt which is formed. Finally, other physical properties such as the creep behavior of rocks are dramatically affected by the presence of small amounts of water.

The presence of hydrated silicates on the Venusian surface was probably first suggested by Mueller (1964a,b). He assumed that the water vapor mixing ratio above the clouds was indicative of that at the surface and then used the spectroscopic data of Bottema *et al* (1964) to set a limit of $P_{\text{H}_2\text{O}} \leq 10^{-3}$ to 10^{-2} bars at the surface. Mueller (1964a) noted that “at 700°K such small quantities of water require that it must almost all be bound as structural water in hydrous phases. The most likely phases to consider are the hydrous silicates such as the amphiboles and micas.” In particular Mueller (1964a) first suggested that a mica mineral, phlogopite might be stable under Venusian surface conditions. However, the lack of thermodynamic data for many hydrated minerals combined with the lack of knowledge about the actual water vapor partial pressure at the Venusian surface prevented Mueller from making any definitive predictions about hydrated silicate stability on Venus.

Problems with unavailable or unreliable thermodynamic data and uncertainty about the actual water vapor content of the lower atmosphere of Venus also plagued the work of subsequent investigators (e.g., Lewis 1968a, 1970a; Lewis and Kreimendahl 1980; Khodakovskiy *et al* 1979; Barsukov *et al* 1980; Volkov *et al* 1986). Thus, the literature is full of conflicting predictions. For example, Lewis (1968a) predicted that muscovite and phlogopite would be present on the surface while Lewis (1970a), Lewis and Kreimendahl (1980), and Nozette and Lewis (1982) calculated that muscovite and phlogopite were unstable and that the amphibole tremolite would be present. Likewise, Khodakovskiy *et al* (1979) predicted the presence of several hydrated minerals (epidote, glaucophane, tremolite, phlogopite, annite) but Khodakovskiy (1982), Barsukov *et al* (1980) and Volkov *et al* (1986) later claimed that *none* of these phases were stable on Venus. However, the Soviet work is contradicted by the prediction of Nozette and Lewis (1982) that tremolite will be stable at high altitudes on the Venusian surface even with only 20 ppm water in the atmosphere. What hydrated silicates (if any) are stable on Venus?

Tremolite[Ca₂Mg₅Si₈O₂₂(OH)₂]. Tremolite is an amphibole and is probably the most frequently suggested hydrated silicate on Venus. In order for tremolite to be stable on Venus, the equilibrium H₂O vapor pressure for the dehydration reaction



must be less than or equal to the H₂O partial pressure in the atmosphere. This critical value is ~ 0.002 bars at the surface of Venus.

Taking thermodynamic data from Robie *et al* (1979), the equilibrium H₂O vapor pressure for reaction (47) is

$$\log_{10} P_{\text{H}_2\text{O}} = 8.05 - 6742(\pm 1334)/T \quad (48)$$

from 600 to 800 K. The corresponding water vapor mixing ratios are tabulated as a function of altitude from 0 to 12 km in Table 4. Over this entire range, tremolite is thermodynamically unstable on the Venusian surface because the amount of water vapor in the atmosphere is several times less than the amount needed for tremolite to be stable. Within the rather large uncer-

Table 4. Minimum Water Concentrations for Tremolite Stability on Venus

Altitude (km)	Temperature (K)	Water Vapor Mixing Ratios and the Range of Values
0	740	915 ppm (15 ppm - 5.8%)
2	725	670 ppm (10 ppm - 4.6%)
4	710	490 ppm (6 ppm - 3.7%)
6	695	340 ppm (4 ppm - 2.9%)
8	679	230 ppm (2.5 ppm - 2.2%)
10	663	150 ppm (1.5 ppm - 1.6%)
12	648	100 ppm (0.9 ppm - 1.2%)

tainties in the thermochemical data, one could conclude that tremolite may be stable over this entire altitude range. However, this conclusion is probably incorrect.

Most of the uncertainty in the calculated equilibrium water vapor pressure arises from the uncertainty in the determination by HF acid solution calorimetry of the heat of formation of tremolite (Weeks, 1956). Robie *et al* (1979) used these data in their compilation. An independent assessment of the thermodynamic properties for tremolite by Helgeson *et al* (1978), who used the results of high pressure phase equilibria experiments (Boyd 1959) instead of the HF acid solution calorimetry work, also indicates that tremolite is unstable on the surface of Venus. In this case, the calculated water vapor mixing ratio needed for tremolite stability is $\sim 2.7\%$ at 740 K and decreases to $\sim 0.4\%$ at 648 K (at 12 km altitude).

Extrapolation of the water vapor mixing ratios in Table 4 to lower temperatures (and thus to higher altitudes) indicates that tremolite should be thermodynamically stable at ~ 14 km and above. For comparison, Nozette and Lewis (1982) concluded that tremolite would be stable at altitudes of 16.3 km and higher. In this regard it is important to remember that the highest point measured on Venus by the Pioneer Venus radar altimeter is ~ 11 km high (Masursky *et al* 1980). However higher elevations are not excluded by the PV radar altimetry which covered only 93% of the planet at low resolution. But in any case from our calculations we can conclude that tremolite is probably unstable on the extensive low-lying regions of the Venusian surface although it may be stable at higher elevations that have a limited areal extent.

However even this conclusion is tentative because of the disagreement between the phase equilibrium data (Boyd 1959) and the calorimetric data (Weeks 1956) on tremolite stability. The thermodynamic predictions could be made more robust by an improved determination of the heat of formation of tremolite or by an improved determination of the temperature dependent equilibrium constant for reaction (47). If tremolite is then found to be stable in elevated regions on Venus it will be important to measure the kinetics of the vapor phase hydration of anhydrous silicates to determine how rapidly water vapor could be depleted by tremolite formation on the surface.

Phlogopite[KMg₃AlSi₃O₁₀(OH)₂]. Phlogopite is a mica, an end-member of a solid solution series involving F – OH – Cl and Fe – Mg exchange. Here, we consider only the Mg – OH end-member, which has often been suggested to be present on the surface of Venus. The stability of an isolated phlogopite grain on the Venusian surface is governed by the dehydration reaction



and the equilibrium water vapor pressure in the 600 to 800 K range is

$$\log_{10}P_{\text{H}_2\text{O}} = 9.50 - 7765(\pm 240)/T. \quad (50)$$

This equation is calculated using thermodynamic data from Helgeson *et al* (1978) for phlogopite and data from Robie *et al* (1979) for the other phases.

Table 5. Minimum Water Concentrations for Phlogopite Stability on Venus

Altitude (km)	Temperature (K)	Water Vapor Mixing Ratios and the Range of Values
0	740	1060 ppm (500 ppm - 2200 ppm)
2	725	730 ppm (340 ppm - 1570 ppm)
4	710	490 ppm (230 ppm - 1070 ppm)
6	695	325 ppm (150 ppm - 720 ppm)
8	679	200 ppm (90 ppm - 460 ppm)
10	663	125 ppm (55 ppm - 280 ppm)
12	648	75 ppm (30 ppm - 180 ppm)

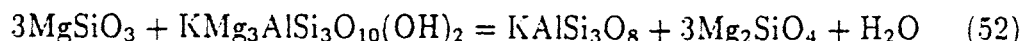
The corresponding water vapor mixing ratios that are required for the stability of isolated phlogopite grains are tabulated in Table 5. We can see that phlogopite, like tremolite, apparently requires water vapor mixing ratios of $\sim 100 - 1000$ ppm to be stable. These values are 5 to 50 times higher than the water vapor content measured by Venera 11/12 and 13/14 near the surface of Venus. Within the formal uncertainties in the thermodynamic data, isolated phlogopite grains apparently could be stable at ~ 12 km and above on Venus.

However, a more recent assessment of the thermodynamic properties of phlogopite by Berman (1988) leads to less negative ΔG_f° values and thus to higher equilibrium water vapor pressures for reaction (49). Using Berman's (1988) phlogopite data instead of the Helgeson *et al* (1978) data, the equilibrium expression for reaction (49) is

$$\log_{10} P_{H_2O} = 8.58 - 6774(\pm 294)/T. \quad (51)$$

At 740 K, the calculated water vapor pressure is ~ 0.27 bars, or about 140 times higher than the Venera measurements indicate. At lower temperatures (i.e., higher altitudes) the equilibrium water vapor pressures calculated from Berman's data are significantly higher than the observed water vapor abundances and than the equilibrium water vapor pressures calculated from Helgeson's data.

However, if solid-solid reactions are sufficiently rapid, the stability of phlogopite will probably be influenced by reactions with other minerals in the surrounding rock. Phlogopite stability in mafic (basaltic) rocks is controlled by the reaction



while phlogopite stability in felsic (granitic) rocks is governed by the reaction



Taking thermodynamic data for phlogopite from Helgeson *et al* (1978) and from Robie *et al* (1979) for the other phases, the equilibrium water vapor

pressures for reactions (52) and (53) are given by

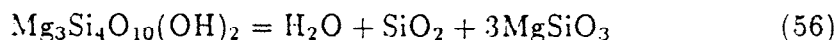
$$\log_{10}P_{\text{H}_2\text{O}} = 8.68 - 6685(\pm 425)/T \quad (54)$$

$$\log_{10}P_{\text{H}_2\text{O}} = 8.48 - 5506(\pm 408)/T \quad (55)$$

respectively. Although the equilibrium expressions show that phlogopite is more stable in mafic rocks than in felsic rocks, the equilibrium water vapor pressures required for phlogopite stability in both rock types are significantly higher than the values near the surface of Venus. Recalculating equations (54) and (55) using Berman's phlogopite data leads to the same conclusion.

We conclude that although phlogopite thermodynamic data from different compilations show surprisingly large differences, phlogopite, like tremolite, cannot exist in low-lying regions on the Venusian surface and if present at all, could only be found in elevated terrain. But we should realize that at these high altitudes (and low temperatures) the kinetics of phlogopite formation by the vapor phase hydration of anhydrous silicates may inhibit phlogopite formation in geologically reasonable times.

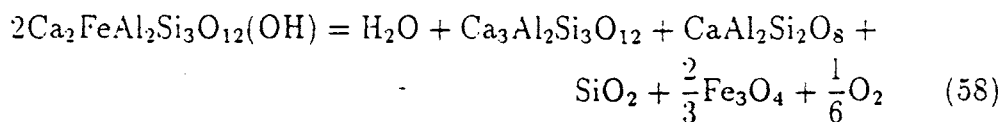
Talc, Epidote, Pargasite, and Muscovite. Talc is a hydrated magnesium silicate, epidote is a hydrated Fe^{3+} -bearing orthosilicate, pargasite is a hornblende in the amphibole group, and muscovite is a mica. These are the only other hydrated silicates (for which thermodynamic data are available) that have equilibrium water vapor pressures less than the total pressure at the Venusian surface. Talc dehydration occurs via the reaction



which has an equilibrium water vapor pressure given by

$$\log_{10}P_{\text{H}_2\text{O}} = 8.58 - 6088(\pm 302)/T \quad (57)$$

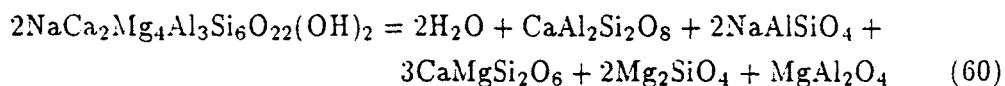
from 600 to 800 K. Epidote dehydration occurs via the reaction



which has an equilibrium constant given by

$$\log_{10}K_{58} = 10.01 - 9634(\pm 437)/T \quad (59)$$

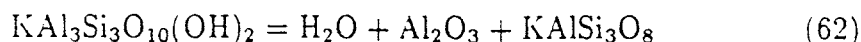
from 600 to 800 K. Pargasite dehydration occurs via the reaction



which has an equilibrium water vapor pressure given by

$$\log_{10}P_{\text{H}_2\text{O}} = 5.04 - 2911(\pm 1728)/T \quad (61)$$

from 600 to 800 K. Muscovite dehydration occurs via the reaction



which has an equilibrium water vapor pressure given by

$$\log_{10} P_{\text{H}_2\text{O}} = 7.80 - 4765(\pm 254)/T \quad (63)$$

from 600 to 800 K. Thermodynamic data from Helgeson *et al* (1978) and Robie *et al* (1979) were used to calculate the equilibrium constants for the dehydration reactions.

In all cases, the water vapor mixing ratios needed for these hydrated silicates to be stable far exceed the observed values. Talc requires $\sim 2\%$ H_2O , pargasite requires $\sim 13\%$ H_2O , and muscovite requires $\sim 24\%$ H_2O to be stable at 740 K. Because it contains Fe, epidote stability depends on both the oxygen fugacity and the water vapor partial pressure. At 740 K, the equilibrium constant K_{58} for epidote dehydration is

$$K_{58} = 10^{-3.009} = P_{\text{H}_2\text{O}} \cdot f_{\text{O}_2}^{1/6} \quad (64)$$

and the corresponding water vapor mixing ratio is $\sim 4\%$ for an oxygen fugacity of $10^{-21.5}$ bars. None of these four minerals are stable at *any* point on the Venusian surface, even when the uncertainties in the thermodynamic data are taken into account.

Other Hydrated Silicates. The other hydrated silicates for which thermodynamic data are available are paragonite, glaucophane, margarite, chrysotile, anthophyllite, prehnite, pyrophyllite, and kaolinite clay. Their equilibrium water vapor pressures at the surface of Venus were calculated using thermodynamic data from literature compilations and the original experimental papers (Robie *et al* 1979; Hemingway *et al* 1982; Robie and Hem-

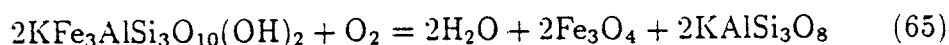
Table 6. Equilibrium Water Vapor Pressures for Hydrated Silicates on the Venus Surface (740 K)

Mineral Name	Ideal Formula	Water Vapor Pressure
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	0.09 bars
Phlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	0.1 bars
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	2 bars
Epidote	$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$	4 bars
Pargasite	$\text{NaCa}_2\text{Mg}_4\text{Al}_3\text{Si}_6\text{O}_{22}(\text{OH})_2$	13 bars
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	23 bars
Paragonite	$\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	110 bars
Glaucophane	$\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$	230 bars
Margarite	$\text{CaAl}_4\text{Si}_2\text{O}_{10}(\text{OH})_2$	240 bars
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	310 bars
Anthophyllite	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	510 bars
Prehnite	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$	610 bars
Pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	620 bars
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	890 bars
Annite	$\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	12,600 bars

ingway 1984; Likhoydov *et al* 1982; Berman *et al* 1986). The results of these calculations, which are summarized in Table 6, show that none of these hydrated silicates can be stable anywhere on the Venusian surface because the equilibrium water vapor pressures exceed the total atmospheric pressure. In this regard we note that anthophyllite, which Mueller (1970) had suggested would be stable, requires $P_{H_2O} \geq 510$ bars to be stable at 740 K on the Venusian surface.

Amphibole and Mica Solid Solutions. Thus our calculations show that no pure hydrated silicates are stable in the extensive low-lying regions on Venus and that only tremolite and phlogopite are possibly stable at elevations exceeding those observed by the PV radar altimeter. However on the Earth amphiboles and micas frequently have complex compositions (Deer *et al* 1963). Two of the observed substitutions that are important here are Fe^{2+} substituting for Mg^{2+} and F^- substituting for OH^- . What are the effects of these substitutions on amphibole and mica stabilities? Unfortunately, this question is difficult to answer because very few thermodynamic data are available on the thermodynamic properties of the Fe-bearing and F-bearing endmember minerals or for the relevant solid solutions.

Annite, which is the Fe-bearing analog of phlogopite, is one mineral for which the necessary data are available. Annite dehydration occurs via the reaction



which has an equilibrium constant

$$K_{65} = P_{H_2O}^2 / f_{O_2} \quad (66)$$

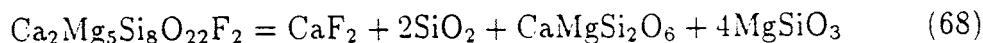
dependent on both the water vapor pressure and the oxygen fugacity. Thermodynamic data from Helgeson *et al* (1978) give the equation

$$\log_{10} K_{65} = 6.45 + 17217(\pm 580)/T \quad (67)$$

and taking $f_{O_2} \sim 10^{-21.5}$ bars yields $P_{H_2O} \sim 10^{4.1}$ bars at 740 K. (Water vapor is certainly non-ideal at these pressures, but inclusion of the proper non-ideality corrections will not alter the conclusion that annite is thermodynamically unstable on the Venusian surface). Thus, annite is much less stable than phlogopite on Venus and any Fe substitution for Mg in phlogopite will actually increase the amount of water vapor required for phlogopite stability on Venus. Likewise, phase diagrams for ferro-actinolite, which is the Fe-bearing analog of tremolite, show that it is less stable than tremolite and decomposes at temperatures about 300° lower than tremolite does at an oxygen fugacity defined by the fayalite-magnetite-quartz buffer (Gilbert *et al* 1982). These phase diagrams indicate that Fe substitution for Mg in tremolite will also decrease tremolite stability on Venus.

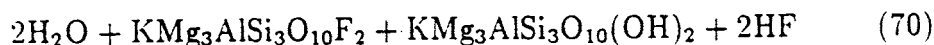
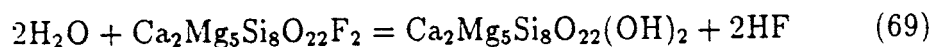
However F substitution for OH in amphiboles has the opposite effect and increases amphibole stabilities (e.g., Gilbert *et al* 1982; Grigoriev and Isküll 1937; Comeforo and Kohn 1954; Valley *et al* 1982; Graham and Navrotsky 1986). For example, the equilibrium temperature ($\Delta G = 0$) for fluor-

tremolite decomposition via the reaction



is $1136 \pm 3^\circ\text{C}$ at 1 bar versus an equilibrium temperature of only 552°C at $P_{\text{H}_2\text{O}} = 1$ bar for the analogous tremolite decomposition reaction (Gilbert *et al* 1982).

Fluor-amphibole and fluor-phlogopite stability is considered in section (2.4.4); these results show that fluor-tremolite, fluor-edenite, and fluor-phlogopite are stable (within the uncertainties in the thermodynamic data) over many altitudes on the Venusian surface. Thus, OH may be present in amphiboles and phlogopite in solid solution with F, but, as shown above, not as hydroxyl end-member minerals. Assuming ideal solid solution of OH- and F-endmembers, we attempted to calculate the mole fractions of dissolved tremolite and phlogopite using the exchange reactions



which have the equilibrium constants

$$\log_{10}K_{69} = -1.46 - 3915(\pm 1167)/T \quad (71)$$

$$\log_{10}K_{70} = -2.44 - 2900(\pm 1840)/T. \quad (72)$$

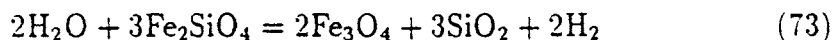
However, the uncertainties in the thermodynamic data for the tremolite and phlogopite exchange reactions are so large that a wide range of tremolite and phlogopite mole fractions up to unity are derived. The calculated minimum mole fractions at 740 K are ~ 0.08 for tremolite and ~ 0.02 for phlogopite. The analogous exchange reaction involving fluor-edenite is not considered because no thermodynamic data are available for edenite.

To summarize, no pure hydrated silicates are thermodynamically stable on the Venusian surface with the possible exceptions of tremolite and phlogopite which may be stable at high altitudes. Although stability of tremolite and phlogopite is possible within the formal uncertainties in the thermodynamic data, it is unlikely. Solid solutions of hydroxy- and fluor-amphiboles, and of hydroxy- and fluor-micas such as tremolite solid solutions with fluor-tremolite and phlogopite solid solutions with fluor-phlogopite may be stable on the Venusian surface, but the uncertainties in the relevant thermodynamic data are too large to permit any definitive predictions from being made at present. High pressure phase equilibrium experiments conducted by experimental petrologists show that some amphibole and hornblende minerals are more stable than those considered here; however, these phases could not be considered because of a lack of thermodynamic data. These minerals include edenite $[\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}(\text{OH})_2]$, some members of the richterite family, and some alkali amphiboles; they are discussed by Gilbert *et al* (1982). Furthermore, as noted above, the existing thermodynamic data for tremolite and phlogopite need to be measured with greater precision to better constrain the stabilities of these minerals on the surface of Venus. Thus, further work on

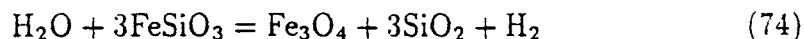
basic thermodynamic data for several amphibole, hornblende, and mica minerals is needed before firm conclusions can be drawn about the stabilities of hydrated silicates on the surface of Venus and their potential as a sink for water vapor.

2.2.3 Molecular Hydrogen

Another proposed sink for water vapor in the lower atmosphere of Venus is the formation of molecular H_2 by the oxidation of Fe-bearing minerals on the surface of Venus. These reactions are exemplified by



between H_2O + fayalite yielding magnetite + quartz + H_2 and by



between H_2O + ferrosilite yielding magnetite + quartz + H_2 .

Thermodynamic data from Robie *et al* (1979) and Helgeson *et al* (1978), give

$$\log_{10}K_{73} = -4.80 + 791(\pm 480)/T \quad (75)$$

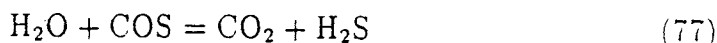
$$\log_{10}K_{74} = -2.56 + 499(\pm 438)/T \quad (76)$$

from 600 to 800 K for the equilibrium constants for reactions (73) and (74). Combining these data with the fayalite and ferrosilite activities calculated earlier, we find that at 740 K the equilibrium H_2 mixing ratio at the Venus surface is only ~ 3 ppb. This is approximately 7200 times lower than the observed H_2O mixing ratio.

In this regard, we also note that two different spacecraft experiments have identified molecular hydrogen on Venus. The first identification was by Kumar *et al* (1981) who interpreted the mass 2 peak observed by the Pioneer Venus Orbiter Ion Mass Spectrometer as H_2^+ and derived an H_2 mixing ratio of 10 ppm at altitudes below 140 km. The second identification was by the Venera 13/14 gas chromatography experiment which supposedly detected 25 ± 10 ppm H_2 in the 49–58 km altitude range (Mukhin *et al* 1983). However, as described earlier, this experiment also detected a similar amount of O_2 in approximately the same altitude range. The similar H_2 and O_2 mixing ratios are thermodynamically inconsistent; one or both must be incorrect. The problems with the carrier gas flow in the Venera 13/14 gas chromatography experiment (Krasnopolsky 1986) lead us to believe that none of the peaks were identified properly. Thus, we also discount the H_2 identification of Mukhin *et al* (1983). However, even if the H_2 mixing ratio of 10 ppm deduced by Kumar *et al* (1981), which is significantly higher than the thermodynamic equilibrium value, can be sustained by disequilibrium chemistry in the lower atmosphere, it is still too low to provide a sink of the required magnitude for water vapor.

2.2.4 Gas Phase Sinks

Hydrogen sulfide. The formation of H_2S via reactions exemplified by



has also been suggested as a sink for water vapor, and apparently received observational support with the reported detection of 80 ± 40 ppm H_2S and 40 ± 20 ppm COS in the 29–37 km altitude range by the Venera 13/14 gas chromatography experiment (Mukhin *et al* 1983). However, problems with the carrier gas flow (Krasnopolsky 1986) during these measurements apparently caused problems with peak identifications for almost all compounds. Thus, the derived COS and H_2S abundances are suspect. Furthermore, Bézard *et al* (1990) have detected COS at a much lower level of ~ 0.3 ppm in the 35–45 km altitude range. Assuming that the COS mixing ratio is constant down to the surface, and using the equilibrium constant

$$\log_{10} K_{77} = -0.15 + 1810(\pm 69)/T \quad (78)$$

for reaction (77), we find that the predicted H_2S mixing ratio is ~ 1 ppb at the surface (740 K). The equilibrium H_2S mixing ratio increases only very slightly with decreasing temperature to ~ 5 ppb at 600 K and is clearly insufficient to serve as a water vapor sink.

Carbonic acid gas. Recently, Lewis and Grinspoon (1990) have suggested that formation of carbonic acid gas via the reaction



serves as a water vapor sink in the lower atmosphere of Venus. On the basis of estimated thermodynamic data, they calculate the equilibrium constant for reaction (79) as

$$\log_{10} K_{79} = 0.43 - 1310/T \quad (80)$$

with an uncertainty of a factor of 2 to 3. Assuming conservation of hydrogen atoms between water vapor and carbonic acid gas, Lewis and Grinspoon then calculate vertical profiles for these species. Figure 7, modified from their paper, shows a representative calculation including H_2SO_4 gas which is also included in their modelling.

The high CO_2 pressure in the lower atmosphere of Venus drives reaction (79) to the right and produces significant amounts of H_2CO_3 gas ($\sim 80\%$ of total hydrogen) at the surface of Venus. The equilibrium H_2O mixing ratio of $\sim 10 \pm 4$ ppm is consistent with the observed value of ~ 20 ppm.

However, the problem with this explanation is that H_2CO_3 gas has not been isolated or characterized spectroscopically, but has only been proposed on the basis of a peak in the mass spectrum of decomposing NH_4HCO_3 solid (Terlouw *et al* 1987). Before this explanation can be accepted, it is clearly necessary to verify the existence of the postulated carbonic acid gas and to quantitatively determine its thermodynamic properties.

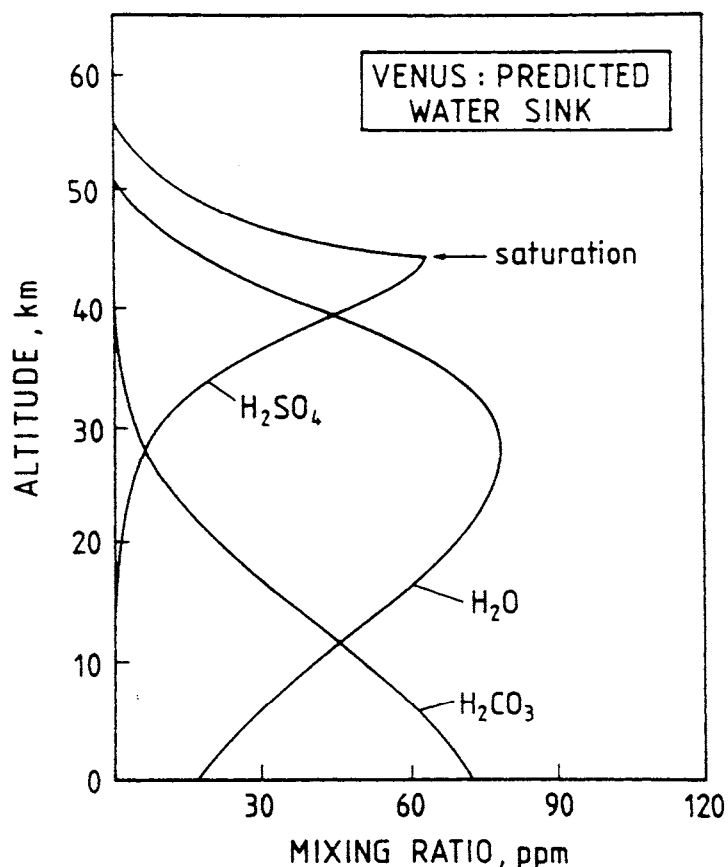


Figure 7. Predicted vertical profiles for H_2O , H_2SO_4 , and H_2CO_3 in the lower atmosphere of Venus (modified from Fig. 1 of Lewis and Grinspoon 1990). Their calculations, based on estimated thermochemical data, predict that the reaction $\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) = \text{H}_2\text{CO}_3(\text{g})$ is driven to the right at the high pressures in the lower atmosphere of Venus and that carbonic acid gas is a sink for water vapor.

2.2.5 Deuterium

Measurements made by the Pioneer Venus ion and neutral mass spectrometers provided the first evidence for deuterated species in the atmosphere of Venus. McElroy *et al* (1982) interpreted the mass 2 peak observed by the Pioneer Venus Orbiter Ion Mass Spectrometer as D^+ and derived a D/H ratio $\sim 10^{-2}$. Subsequently, Hartle and Taylor (1983) derived a D/H ratio of $2.2(\pm 0.6) \times 10^{-2}$ from the same data. Within the uncertainties, both values are approximately 100 times higher than the terrestrial value of $\sim 1.6 \times 10^{-4}$ (Craig, 1961). However, the identification of the mass 2 peak as D^+ is not unique and Kumar *et al* (1981) identified the same peak as H_2^+ .

Donahue *et al* (1982) showed that the data obtained by the PV Large Probe Neutral Mass Spectrometer during the time the inlet was clogged (presumably by sulfuric acid cloud droplets) are consistent with a Venusian D/H ratio $\sim 1.6 \times 10^{-2}$. However, this analysis was questioned by Bertaux and Clarke (1989) who used an upper limit on deuterium Lyman- α emission obtained from the International Ultraviolet Explorer satellite to derive $\text{D}/\text{H} < 5 \times 10^{-3}$ for Venus.

Deuterated water vapor HDO was detected by infrared spectroscopy (at $3.6 \mu\text{m}$) in the Venusian atmosphere by DeBergh *et al* (1989) who found a HDO mixing ratio of ~ 0.1 ppm above the clouds. When combined with previous H_2O observations (e.g., Barker 1975; Fink *et al* 1972) a D/H value at least 3 times greater than the terrestrial value was implied.

More recently, DeBergh *et al* (1990) have observed HDO and H_2O on the night side of Venus at $2.3 \mu\text{m}$, which probes the Venusian atmosphere in the 35 to 45 km altitude region (Bézard *et al* 1990). They find an HDO mixing ratio of 1.3 ± 0.2 ppm and an H_2O mixing ratio of 34 ± 10 ppm, corresponding to $\text{D}/\text{H} = (1.9 \pm 0.6) \times 10^{-2}$, or 120 ± 40 times the terrestrial value, in agreement with the determination by Donahue *et al* (1982).

Deuterated water HDO is the major deuterium reservoir in the atmosphere of Venus. However, exchange of deuterium in this reservoir with hydrogen combined in other gases via equilibria such as

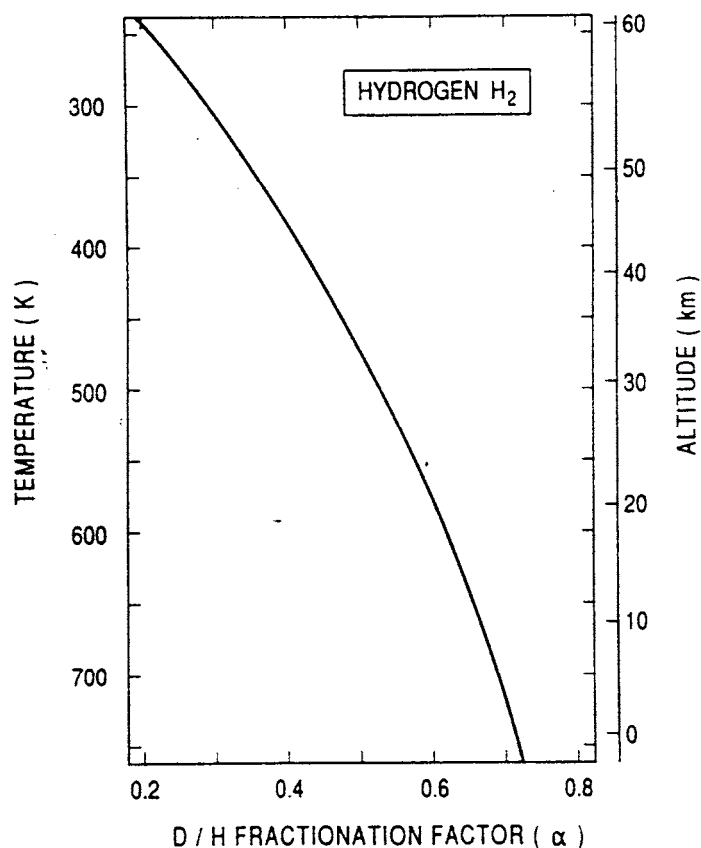
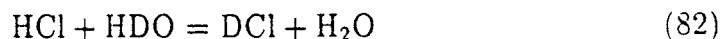
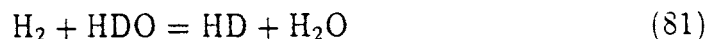
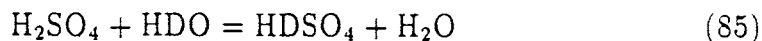
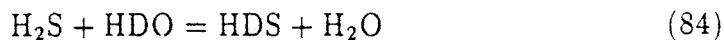


Figure 8. Predicted thermochemical fractionation factors (α) for deuterium exchange between $\text{H}_2 + \text{H}_2\text{O}$ in the atmosphere of Venus. The fractionation factor is defined as the D/H atom ratio in H_2 relative to the D/H atom ratio in H_2O and is tabulated as a function of temperature by Richet *et al* (1977). Hydrogen is predicted to be less enriched in deuterium than is water vapor.



leads to the production of other, less abundant deuterium-bearing gases.

Fegley (1989) calculated the deuterium fractionation factors for several gases (DF, DCl, HDS, HD) as a function of temperature and altitude by using thermodynamic data tabulated by Richet *et al* (1977). The results of these calculations are displayed in Figures 8–11. The deuterium fractionation factor α is defined as

$$\alpha_{\text{gas}} = [(\text{D}/\text{H})_{\text{gas}}]/[(\text{D}/\text{H})_{\text{H}_2\text{O}}] \quad (86)$$

and is related to the abundances of the different deuterated gases by equations such as

$$\text{HD}/\text{H}_2 = \text{HDO}/\text{H}_2\text{O} \cdot \alpha_{\text{H}_2} \quad (87)$$

$$\text{DCl}/\text{HCl} = \text{HDO}/\text{H}_2\text{O} \cdot 2\alpha_{\text{HCl}} \quad (88)$$

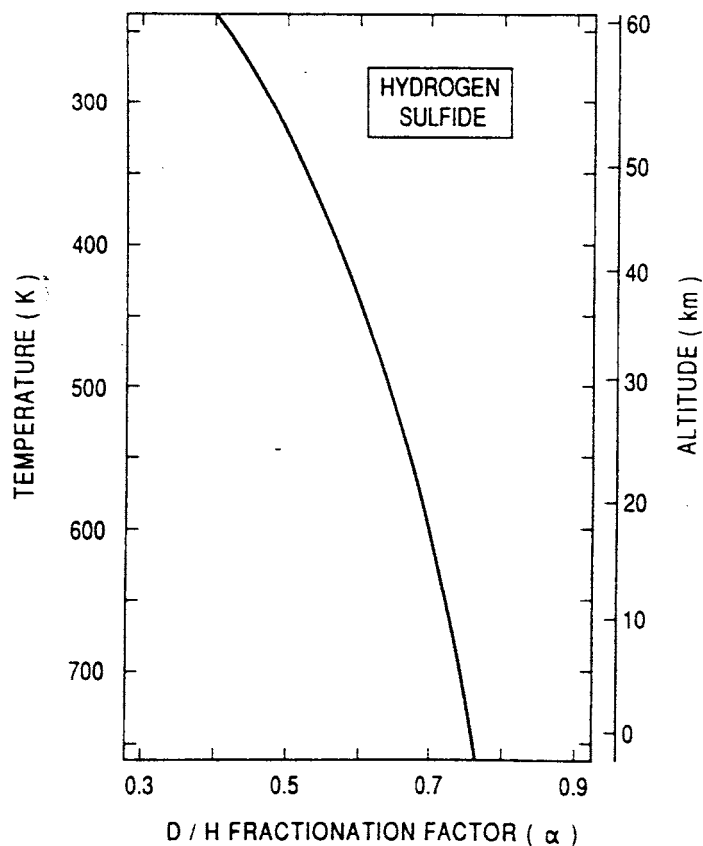


Figure 9. Predicted thermochemical fractionation factors (α) for deuterium exchange between $\text{H}_2\text{S} + \text{H}_2\text{O}$ in the atmosphere of Venus. Hydrogen sulfide is predicted to be less enriched in deuterium than is water vapor.

$$\text{DF/HF} = \text{HDO/H}_2\text{O} \cdot 2\alpha_{\text{HF}} \quad (89)$$

$$\text{HDS/H}_2\text{S} = \text{HDO/H}_2\text{O} \cdot \alpha_{\text{H}_2\text{S}} \quad (90)$$

The equilibrium abundances of these deuterated species calculated from the α values in Figures 8-11 are predicted to be substantial, especially if the deuterium exchange equilibria are established at the Venusian surface where the gas phase reactions may be catalyzed by Fe-bearing minerals. For example, the predicted DCl/HCl ratio is $\sim 3\%$ if reaction (82) is quenched at the surface (740 K) and DCl/HCl is $\sim 1\%$ if reaction (82) is quenched at the cloudtops (250 K). The upper limit of $<8\%$ for DCl/HCl reported by Buie *et al* (1982) is consistent with these predictions and suggests that more sensitive observations of DCl, DF, etc. are worth pursuing in order to obtain independent estimates of D/H on Venus.

2.3 Sulfur-Bearing Gases and Minerals

2.3.1 Atmospheric Abundances of Sulfur Gases

Sulfur dioxide was discovered on Venus by three different groups at about the same time (Barker 1979; Conway *et al* 1979; Stewart *et al* 1979). Their

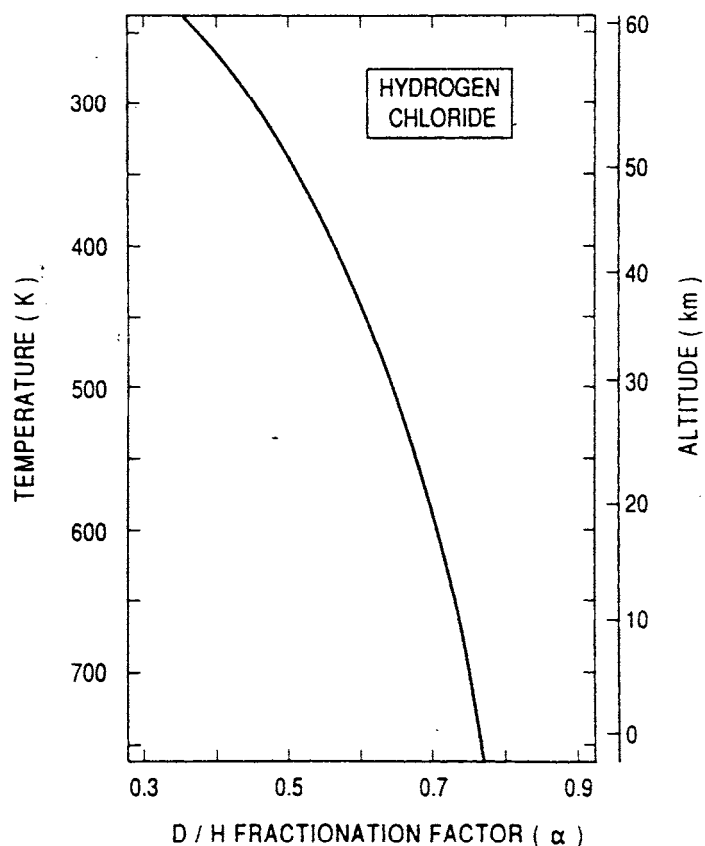


Figure 10. Predicted thermochemical fractionation factors (α) for deuterium exchange between $\text{HCl} + \text{H}_2\text{O}$ in the atmosphere of Venus. Hydrogen chloride is predicted to be less enriched in deuterium than is water vapor.

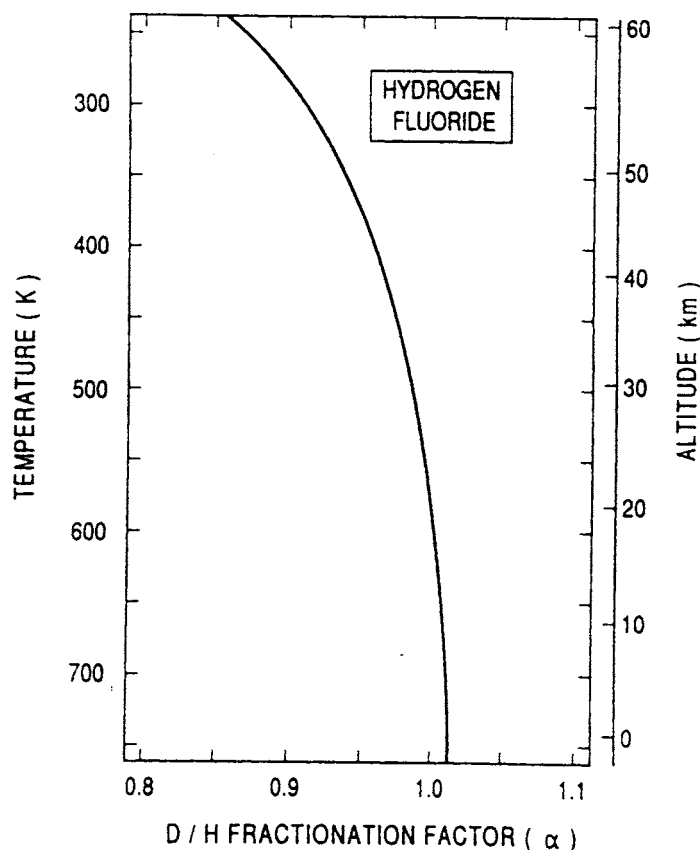


Figure 11. Predicted thermochemical fractionation factors (α) for deuterium exchange between $\text{HF} + \text{H}_2\text{O}$ in the atmosphere of Venus. Hydrogen fluoride is predicted to be equally or more enriched in deuterium than is water vapor.

ultraviolet spectra of the region above the clouds showed SO_2 mixing ratios of <20 ppb to ~ 600 ppb with higher values being observed for longer path lengths in the Venusian atmosphere. As noted by Barker (1979) this behavior is consistent with photochemical destruction of SO_2 in the upper atmosphere of Venus (e.g., as modelled by Winick and Stewart 1980). Subsequent long-term observations of SO_2 by Esposito and colleagues (Esposito 1984; Esposito *et al* 1988; Na *et al* 1990) show a decline in SO_2 mixing ratios above the clouds from 380 ± 80 ppb in 1978 to 50 ± 20 ppb in 1986. This decrease is also consistent with the photochemical destruction of SO_2 to form H_2SO_4 cloud particles. The higher SO_2 mixing ratios observed in 1978-79 are also interpreted as evidence for an injection of SO_2 into the Venus upper atmosphere by active volcanism (Esposito 1984).

The first observations of SO_2 below the clouds were made by Pioneer Venus and Venera 11/12. The Pioneer Venus gas chromatography experiment observed 185 ± 43 ppm SO_2 at 22 km altitude (Oyama *et al* 1980). The Venera 11/12 gas chromatography experiment reported 130 ± 35 ppm SO_2 in the 0-42 km altitude range (Gel'man *et al* 1979). The only subsequent measurement of SO_2 below the clouds is that of Berto *et al* (1987) who reported 30-50 ppm SO_2 in the 25-40 km altitude range from the scanning spectrophotometer experiment on the Vega 1/2 spacecraft. If correct, these

data may indicate an approach towards gas phase thermochemical equilibrium between reduced and oxidized sulfur gases in the lower atmosphere of Venus. However, the results of Berto *et al* (1987) also indicate significant supersaturation of elemental sulfur vapor and must be interpreted with caution. Finally, Steffes *et al* (1990) used Earth-based microwave observations to derive model-dependent upper limits on the SO₂ abundance below the clouds. This is done by analyzing the continuum absorption in the microwave spectra. Steffes *et al* (1990) interpreted their upper limits as showing a decrease in SO₂ below the values measured earlier, but in fact their upper limits are generally consistent (within the uncertainties) with the earlier Pioneer Venus and Venera 11/12 observations.

The other sulfur-bearing gases which have been reported in the atmosphere of Venus are SO, COS, H₂S, H₂SO₄, and elemental sulfur S_x. Na *et al* (1990) discovered SO on Venus. Their ultraviolet observations yield 20±10 ppb SO above the clouds. Carbonyl sulfide COS was first unambiguously observed by Bézard *et al* (1990) in their 2.3μm observations of the night side of Venus. They found ~0.3 ppm COS in the 35-45 km altitude region. A preliminary detection of 3±2 ppm H₂S below 20 km altitude was reported by Hoffman *et al* (1980a) and an upper limit of 2 ppm H₂S was reported by the Pioneer Venus gas chromatography experiment at 22 km altitude (Oyama *et al* 1980). Sulfuric acid vapor has not been observed spectroscopically, but Steffes *et al* (1990) have interpreted the continuum absorption in their microwave spectra as requiring a few ppm gaseous H₂SO₄. This is consistent with the extensive evidence showing that aqueous sulfuric acid droplets constitute the spherical mode 2 cloud particles (Esposito *et al* 1983). Elemental sulfur vapor is interpreted to be the source of the strong absorptions observed in the 450 to 600 nm wavelength region by the scanning spectrophotometer experiment on the Venera 11/12 spacecraft (Moroz *et al* 1979, 1980). San'ko (1980) analyzed these observations and calculated the abundance of the different elemental sulfur vapor species assuming gas phase thermodynamic equilibrium between them. He found a total elemental sulfur mixing ratio (S_x, x = 1-8) of ~20 ppb in the 0-50 km altitude region with S₂ being dominant below ~30 km. Zolotov (1985) redid these calculations and obtained generally similar results to those of San'ko (1980). The Moroz *et al* (1979, 1980) data and the models of San'ko (1980) and Zolotov (1985) rule out the much higher (~0.6%) elemental sulfur mixing ratios proposed by Young (1979) to explain earlier Venera photometer data. As noted above, Berto *et al* (1987) attributed absorption in the 220 to 370 nm wavelength region to elemental sulfur vapor. They obtained much higher mixing ratios of 2-10 ppm for sulfur vapor in the 25-40 km altitude range. This is 200-500 times greater than the total sulfur mixing ratio derived by San'ko (1980). The reasons for these differences, which may represent temporal and/or spatial variations in sulfur chemistry or simply data analysis problems, are unclear.

Finally, the Venera 13/14 gas chromatograph experiment also claimed the detection of 80±40 ppm H₂S and 40±20 ppm COS in the 29-37 km altitude region and 0.2 ppm SF₆ in the 35-58 km altitude region (Mukhin *et al* 1983). However, as noted earlier, problems with the carrier gas flow during the

measurements (Krasnopolsky 1986) apparently caused problems with peak identifications for many compounds. Furthermore, the COS measurement conflicts with the much lower COS mixing ratio observed by Bézard *et al* (1990) in the same altitude region and the H₂S measurement conflicts with the earlier Pioneer Venus results. If, as discussed later in sections (2.3.4) and (2.3.5), COS is produced by pyrite weathering, the fast rate of this reaction (Fegley and Treiman 1990) is predicted to lead to short-term variations in the spatial and temporal abundances of COS in the lower atmosphere of Venus. Likewise, oxidation of mm-sized pyrrhotite grains, such as commonly found in terrestrial basalts, is also relatively rapid (Treiman and Fegley 1991) and short-term variations in COS may also occur as a result of this process. However, the apparent instrumental problems with the Venera 13/14 gas chromatography experiment lead us to assume that the Venera 13/14 results for H₂S and COS are incorrect and we will not use them as constraints on Venus sulfur chemistry. Also, we note that the SF₆ measurement is apparently inconsistent with observed abundances of HF, H₂O, and SO₂ and we discuss it later in connection with halogen-bearing gases.

To summarize this section, we interpret the Earth-based and spacecraft observations of sulfur gases in the lower atmosphere of Venus as showing that SO₂ is the dominant sulfur-bearing gas and that reduced sulfur gases such as COS, H₂S, and elemental sulfur vapor are minor species that constitute $\leq 2\%$ of total gaseous sulfur. However, we also note that if *all* Earth-based and spacecraft observations are taken at face value, a different picture emerges in which the sulfur chemistry of the lower atmosphere is rapidly cycling between dominance by oxidized and reduced sulfur gases. In this picture, which we do not endorse, the Pioneer Venus and Venera 11/12 observations indicate dominance by SO₂ (1978), the Venera 13/14 observations indicate dominance by COS + H₂S (1982), the Vega 1/2 observations indicate dominance by SO₂ but at reduced levels and increased levels of elemental sulfur vapor (1986), the Earth-based microwave observations of Steffes *et al* (1990) indicate SO₂ upper limits similar to the Vega 1/2 observations (1986), and the Earth-based infrared observations of Bézard *et al* (1990) indicate only minor levels of COS (1989). Although this picture cannot be unambiguously ruled out, and although there may be some observational evidence for temporal and/or spatial variations in abundances of SO₂ and COS, we feel that at present the Pioneer Venus, Venera 11/12, and the Earth-based observations (Bézard *et al* 1990) of SO₂ and COS are the most reliable and we use these results as the basis for our discussion of sulfur chemistry.

2.3.2 Abundance of Sulfur on Venus and Earth

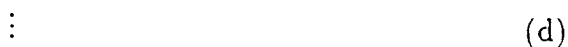
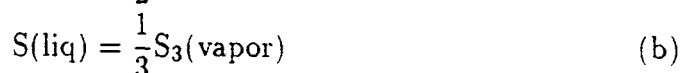
The observations reviewed above indicate that the dominant sulfur-bearing gas in the lower atmosphere of Venus is SO₂. The mean SO₂ mixing ratio of ~ 150 ppm calculated from the Pioneer Venus and Venera 11/12 gas chromatograph experiments (e.g., von Zahn *et al* 1983) corresponds to a column density of $\sim 2.2 \times 10^{23}$ sulfur atoms cm⁻². In comparison, the major sulfur-bearing gases in the terrestrial nonurban troposphere and their mixing ratios (Prinn and Fegley 1987) are COS (0.5 ppb), (CH₃)₂S (~ 0.4 ppb), SO₂ (~ 0.3

ppb), and H_2S (~ 0.2 ppb). The corresponding column density for total sulfur is $\sim 2.0 \times 10^{16}$ atoms cm^{-2} , or about 10^7 times smaller than in the atmosphere of Venus. However, the total amount of sulfur in the Earth's crust (Ronov and Yaroshevsky 1976) and oceans (Turekian 1969) corresponds to $\sim 1.3 \times 10^{26}$ sulfur atoms cm^{-2} , or ~ 600 times larger than total atmospheric sulfur on Venus. This comparison suggests that the high surface temperature on Venus has driven at least some of the sulfur, which would normally be in the crust, into the atmosphere. Furthermore, the high surface temperature may also allow interactions between sulfur-bearing gases in the atmosphere and reactive minerals on the surface of Venus.

2.3.3 Equilibria Between Sulfide and Sulfate Minerals

Sulfur chemistry on Venus is a complex and controversial topic, in part because both oxidized and reduced sulfur-bearing gases such as SO_2 , H_2S , and COS need to be considered, but also because of the sometimes contradictory measurements of sulfur gas abundances. The possible presence of both sulfide and sulfate minerals on the surface of Venus is another complicating factor which needs to be considered.

Mueller (1965) presented the first theoretical models of sulfur chemistry on Venus; however, he neglected COS in his calculations and no observations or upper limits for COS , H_2S , or SO_2 were available for comparison with his results. Despite these problems, his treatment is useful for understanding the complex features of gas-solid reactions involving sulfur. Following Mueller (1965), we begin by considering sulfur chemistry in the absence of other rock-forming elements. The sulfur melting point is 388 K; thus any elemental sulfur on the surface would be liquid and would either evaporate or be oxidized by reaction with CO_2 in the overlying atmosphere. Evaporation would occur via reactions such as

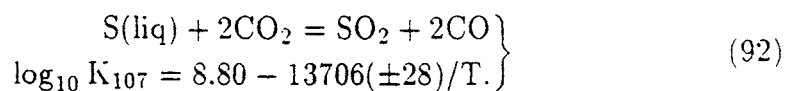


The saturated vapor pressure over liquid sulfur is given by the equations

$$\left. \begin{aligned} P_{\text{vap}} &= P_{\text{S}_2} + P_{\text{S}_3} + \cdots + P_{\text{S}_8} \\ \log_{10} P_{\text{vap}} &= 4.56 - 3286/T. \end{aligned} \right\} \quad (91)$$

calculated from data in Rau et al (1973) and Mills (1974). At 740 K the sulfur vapor pressure is about 1.3 bars, which is substantially greater than the S_2 partial pressure deduced from the Venera 11/12 measurements. Thus, liquid sulfur should rapidly evaporate under Venusian surface conditions.

Oxidation should also occur via reactions such as



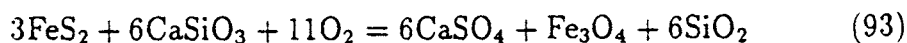
However, removal of liquid sulfur by oxidation is less effective and liquid sulfur could be in equilibrium with 150 ppm SO₂ at all altitudes above ~8.5 km (T < 675 K) on Venus. At these altitudes the saturated vapor pressure is also slightly lower (~0.5 bars at 675 K).

In this regard it is interesting to note that sulfur magmas have been suggested (as an alternative to carbonatite magmas) to explain some of the geologic features observed by the Magellan spacecraft (Kargel et al 1991). If these were erupted at high altitudes the sulfur magma would be stable against oxidation. The presence of other components in the magmas would also probably lower the thermodynamic activity and hence the saturated vapor pressure of the liquid sulfur. For now we conclude that although liquid sulfur may be present transiently on the Venusian surface, it is more likely that sulfur will be present instead in sulfide and/or sulfate minerals of rock-forming elements such as Fe, Ca, Mg, etc.

The distribution of sulfur between sulfide and sulfate minerals depends on the oxidation state of the Venus surface as well as on the abundance of sulfur relative to other elements. As seen from Table 2, the Venera 13/14 and Vega 2 analyses indicate that sulfur is less abundant than other elements such as Fe, Mg, and Ca with which it can react to form sulfides and sulfates. Thus, under sufficiently reducing conditions sulfur will be present in sulfides while under sufficiently oxidizing conditions sulfur will be present in sulfates.

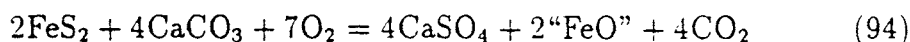
The most common sulfides on Earth are pyrrhotite (FeS to Fe_{1-x}S where x ~0-0.125), pyrite (FeS₂), and pentlandite; other sulfides are only stable under conditions far more reducing than those on Venus or involve other less abundant elements such as Cu, Zn, or Pb. Troilite (FeS) is stable under slightly more reducing conditions and pyrite is stable under slightly more oxidizing conditions; thus the most common sulfide on Venus is expected to be pyrite. No Ni was reported in the Venera 13/14 and Vega 2 analyses, but if, as is likely on cosmochemical grounds, the Venusian Fe/Ni ratio is similar to that on Earth, Ni will be a few % of Fe. Thus, Ni-bearing sulfides will be of secondary importance. Likewise, the most common sulfates on the Earth are anhydrite (CaSO₄) and gypsum (CaSO₄ · 2H₂O); other sulfates involve trace elements such as Ba and Sr, or are less common (Deer *et al* 1963). Thus, by analogy with the Earth, the most common sulfate on Venus is expected to be anhydrite. Thermodynamic data (DeKock 1986) show that gypsum is thermodynamically unstable under Venus surface conditions and it will rapidly dehydrate to form anhydrite.

The transition between pyrite and anhydrite can be calculated from equilibria such as

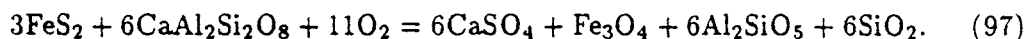
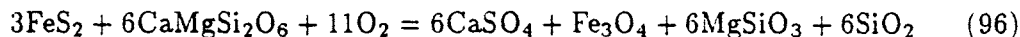
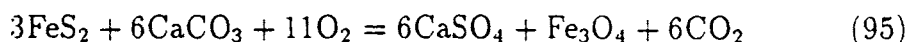


originally proposed by Mueller (1965), or from the pyrite, calcite, anhydrite,

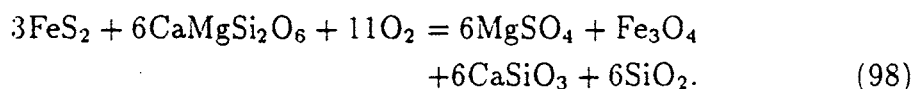
wüstite (PCAW) buffer



originally proposed by Lewis and Kreimendahl (1980), or from the analogous reactions



Equation (95) is a modification of the PCAW buffer of Lewis and Kreimendahl (1980) and equations (96) and (97) exemplify sulfide/sulfate equilibria involving common igneous minerals such as pyroxenes and plagioclase. A related reaction forming MgSO_4 , is



Using data from Robie *et al* (1979), Hemingway *et al* (1982), and the JANAF Tables (Chase *et al* 1985), the equilibrium constants for these reactions are

$$\log_{10}K_{93} = -95.21 + 252320(\pm 1460)/T \quad (99)$$

$$\log_{10}K_{94} = -27.01 + 140256(\pm 966)/T \quad (100)$$

$$\log_{10}K_{95} = -47.04 + 225702(\pm 1412)/T \quad (101)$$

$$\log_{10}K_{96} = -93.42 + 243784(\pm 3212)/T \quad (102)$$

$$\log_{10}K_{97} = -102.56 + 250609(\pm 1574)/T \quad (103)$$

$$\log_{10}K_{98} = -92.96 + 217003(\pm 7181)/T. \quad (104)$$

Table 7 lists the equilibrium oxygen fugacities for reactions (93) – (98) at 740 K; following Lewis and Kreimendahl (1980) the f_{O_2} value for the PCAW buffer is calculated assuming a wüstite thermodynamic activity of 10^{-3} . These results show several important points, foremost of which is that the equi-

Table 7. Sulfide/Sulfate Equilibria on the Surface of Venus

Mineral Assemblage	Equilibrium $\log_{10}f_{\text{O}_2}$ Value
py + wo + mag + anh + qtz	-22.3 ± 0.2
py + cal + anh + wü	-23.0 ± 0.2
py + cal + anh + mag	-22.4 ± 0.2
py + dp + anh + mag + en + qtz	-21.5 ± 0.4
py + an + anh + mag + ad + qtz	-21.5 ± 0.4
py + dp + MgSO_4 + mag + wo + qtz	-19.2 ± 0.4

Abbreviations: py = pyrite, wo = wollastonite, mag = magnetite, anh = anhydrite, qtz = quartz, cal = calcite, wü = wüstite, dp = diopside, en = enstatite, an = anorthite, ad = andalusite

librium oxygen fugacity for coexistence of pyrite + anhydrite depends on the mineral assemblage being considered. In the case of assemblages involving common igneous minerals such as diopside and anorthite, pyrite + anhydrite coexist at the f_{O_2} defined by the CO/CO₂ ratio in the Venusian atmosphere, while, as illustrated in Figure 5, other assemblages involving wollastonite (e.g., Mueller's sulfide/sulfate buffer) or calcite (e.g., Lewis and Kreimendahl's PCAW buffer) are in equilibrium under more reducing conditions. Lewis and Kreimendahl (1980) interpreted the PCAW buffer as an oxygen fugacity buffer for the atmosphere of Venus; we feel that this is unlikely because the calculated f_{O_2} is less than the f_{O_2} fixed by the atmospheric CO/CO₂ ratio. Indeed it is unlikely that any of the sulfide – sulfate reactions are f_{O_2} buffers. The results simply illustrate that under Venus surface conditions pyrite + anhydrite can coexist in some mineral assemblages but not in others.

Now that we know the conditions under which sulfur could be present as sulfide and sulfate on Venus, it is interesting to ask how these minerals will interact with the overlying atmosphere.

2.3.4 Thermodynamics of Pyrite Chemical Weathering on Venus

As first shown by Lewis (1968a, 1970a, 1971b, 1974) and later reinforced by the results of Barsukov *et al* (1982), Khodakovsky (1982), Nozette and Lewis (1982), and Volkov [(1983) reproduced in Volkov *et al* (1986)], at the mean Venus surface temperature of ~740 K, iron sulfides should spontaneously react with the CO₂, CO, and H₂O in the atmosphere of Venus to produce the reduced sulfur gases COS and H₂S. The reactions studied by Lewis (1968a, 1970a) generally involved troilite; however, similar reactions exemplified by

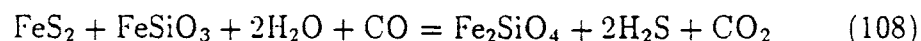
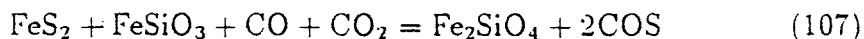
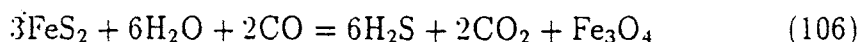


Table 8. Equilibrium Abundances of COS Produced by Pyrite Weathering

Altitude (km)	Temperature (K)	COS Mixing Ratios and the Range of Values		
-4	770	30 ppm	(24 ppm - 38 ppm)	
-2	755	25 ppm	(20 ppm - 32 ppm)	
0	740	21 ppm	(16 ppm - 26 ppm)	
2	725	17 ppm	(13 ppm - 21 ppm)	
4	710	14 ppm	(11 ppm - 17 ppm)	
6	695	11 ppm	(8 ppm - 14 ppm)	
8	679	8 ppm	(6 ppm - 11 ppm)	
10	663	6 ppm	(5 ppm - 8 ppm)	
12	648	5 ppm	(4 ppm - 6 ppm)	

which have the equilibrium constants

$$\log_{10}K_{105} = 7.48 - 19334(\pm 441)/T \quad (109)$$

$$\log_{10}K_{106} = 6.91 - 8726(\pm 360)/T \quad (110)$$

$$\log_{10}K_{107} = 2.66 - 5902(\pm 211)/T \quad (111)$$

$$\log_{10}K_{108} = 2.43 - 2345(\pm 215)/T \quad (112)$$

are responsible for the chemical weathering of pyrite on the surface of Venus.

Using the equilibrium constant expressions above, the COS and H₂S abundances resulting from pyrite weathering were calculated as a function of altitude on the surface of Venus. The results, which are listed in Tables 8 and 9, show that pyrite weathering on the Venus surface should produce COS mixing ratios of ~5–30 ppm, substantially larger than the observed value of ~0.3 ppm (Bézard *et al* 1990) and H₂S mixing ratios of ~40–100 ppb, substantially smaller than the preliminary value of 3±2 ppm obtained by the Pioneer Venus mass spectrometer (Hoffman *et al* 1980), and in agreement with the upper limit of 2 ppm from the Pioneer Venus gas chromatography experiment (Oyama *et al* 1980). The results given in the tables are for reactions (105) and (106); however, virtually identical COS and H₂S abundances are produced from reactions (107) and (108).

Lewis (1968a, 1970a) obtained very similar COS abundances of ~50 ppm but substantially larger H₂S abundances of ~5 ppm. As can be seen by inserting Lewis' assumed mixing ratios into the equilibrium constant expression for equation (106), the larger H₂S mixing ratio is simply due to the much larger H₂O mixing ratio of ~1000 ppm which he used. Lewis (1968a, 1970a) noted that his predicted COS and H₂S mixing ratios exceeded the upper limits of ~10⁻⁶ and ~3 × 10⁻⁷, respectively, set by Earth-based spectroscopy (Cruikshank 1967; Anderson *et al* 1969; Kuiper 1971) and explained the absence of COS and H₂S from the observable regions of Venus' atmosphere by the precipitation of HgS (cinnabar) at lower levels (Lewis 1969, 1970b). Mercury is highly volatile and if present at terrestrial abundance in Venus would be totally outgassed into the atmosphere (Lewis 1969; Barsukov *et al* 1981; Khodakovsky 1982), and available for reaction with COS and H₂S.

Table 9. Equilibrium Abundances of H₂S Produced by Pyrite Weathering

Altitude (km)	Temperature (K)	H ₂ S Mixing Ratios and the Range of Values
-4	770	100 ppb (84 ppb - 120 ppb)
-2	755	92 ppb (77 ppb - 111 ppb)
0	740	84 ppb (70 ppb - 102 ppb)
2	725	77 ppb (64 ppb - 93 ppb)
4	710	70 ppb (57 ppb - 85 ppb)
6	695	63 ppb (52 ppb - 77 ppb)
8	679	56 ppb (46 ppb - 69 ppb)
10	663	50 ppb (40 ppb - 62 ppb)
12	648	44 ppb (36 ppb - 55 ppb)

Neither Hg nor any other Hg-bearing compounds have been detected in the lower atmosphere of Venus and the upper limit on Hg compounds is <5 ppm (Hoffman *et al* 1980a). Thus, Lewis' model is quantitatively inapplicable to COS chemistry but it still may be useful for discussions of the abundances of highly volatile elements on Earth and Venus.

2.3.5 Kinetics of Pyrite Chemical Weathering on Venus

Alternatively, pyrite weathering may be a relatively slow process so that chemical equilibrium is not attained and thus, the predicted COS mixing ratio is never reached. Indeed, the pre-Magellan radar observations of Venus apparently provided support for this scenario. Pettengill *et al* (1982, 1983, 1988) and Jurgens *et al* (1988, 1989) observed radar "bright" regions in the Venus highlands and lowlands that they suggested are pyrite. Furthermore, Jurgens *et al* (1988) concluded that the radar "bright" material is chemically stable on the surface of Venus. Assuming that 25% of the craters have "bright" ejecta and that the mean surface age is $\sim 10^9$ years, Jurgens *et al* (1988) speculated "that weathering to reduce brightness takes about 250 million years." If this material were pyrite, as believed by some prior to the Magellan observations, then the equilibrium concentration of COS would never be attained and the discrepancy between the thermodynamic predictions and spectroscopic upper limits would be resolved.

However, exactly the opposite situation is indicated by the recent experimental measurements of Fegley and Treiman (1990) on the rate of pyrite chemical weathering on the surface of Venus. They found that pyrite oxidation to magnetite is a rapid reaction with a temperature-dependent rate (R) given by

$$R = 10^{24.20(\pm 0.70)} \exp[-13,080(\pm 1380)]/T \quad (113)$$

which has units of S atoms $\text{cm}^{-2} \text{sec}^{-1}$ and an activation energy of 108.7 ± 11.4 kJ mole^{-1} . Taking into account the surface area distribution as a function of altitude on Venus, Fegley and Treiman (1990) calculated a global mean rate of $\sim 3.1 \times 10^{16}$ S atoms $\text{cm}^{-2} \text{sec}^{-1}$, corresponding to the weathering of ~ 20 cm of pyrite per year. At higher elevations, such as on Maxwell Montes, the lower temperature of ~ 665 K leads to a lower pyrite weathering rate of ~ 3 cm per year.

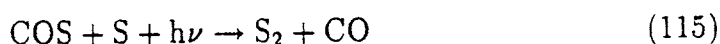
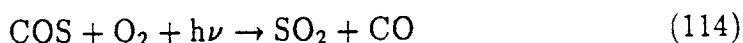
In other words, pyrite weathering on Venus is a rapid reaction. One implication of this result is that the radar "bright" materials in the highlands and in the lowlands are probably not pyrite. The preliminary results of Treiman and Fegley (1991) on the rate of pyrrhotite oxidation show that mm-sized pyrrhotite grains are rapidly weathered on the Venus surface and are also unlikely candidates for the radar "bright" materials. But the preliminary results of Treiman and Fegley (1991) also show that massive pyrrhotite deposits, such as the magmatic sulfide deposits on the Earth are more resistant to weathering and may persist for geologically long periods. However, as noted by Fegley and Treiman (1990) magnetite, which is the weathering product of pyrite and pyrrhotite oxidation, is chemically stable on the

surface of Venus and is also a radar "bright" material (e.g., Pettengill *et al* 1988). Thus, solely on geochemical grounds, Fe-bearing oxides such as magnetite are better candidates for the radar "bright" materials on the surface of Venus. However, these geochemical arguments still do not resolve the separate question of whether or not the volume fractions (up to 14%) proposed by Pettengill *et al* (1988) for the abundance of the radar "bright" materials are reasonable. Indeed in this regard we note that such high contents of opaque minerals (i.e., oxides, sulfides) are uncommon in most terrestrial basalts and are apparently found only in special materials such as magmatic sulfide deposits on the Earth and the ilmenite rich basalts on the Moon.

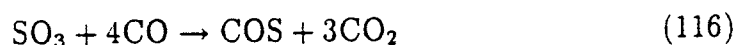
2.3.6 COS Gas Phase Chemistry

Another implication of the kinetic studies of pyrite and pyrrhotite oxidation is that the equilibrium abundance of COS can rapidly be produced by sulfide chemical weathering. However, in the absence of any destruction mechanism, the COS abundance in the lower atmosphere of Venus would then be expected to be approximately 20–100 times larger than that observed by Bézard *et al* (1990). How can this discrepancy be explained?

One possible explanation is that no sulfides are ever exposed on the Venusian surface, and thus no sulfide chemical weathering takes place. However by analogy with the Earth, we argue that this possibility, although it cannot be unambiguously ruled out, is unlikely. Another possible explanation, which is illustrated in Figure 36 of von Zahn *et al* (1983), is that COS is photochemically converted to SO₂ and/or elemental sulfur vapor by photochemical reactions in the lower atmosphere of Venus at ~30 km altitude. These proposed transformations are exemplified by the net reactions



which are disequilibrating reactions driven by sufficiently energetic solar ultraviolet photons below the clouds. However, as also postulated in von Zahn *et al* (1983), these disequilibrating reactions are opposed by thermochemical reactions such as

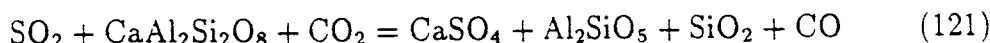
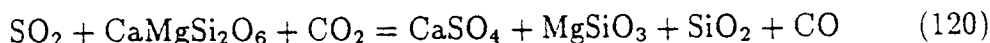
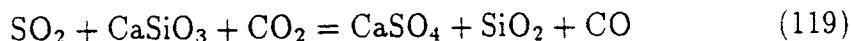
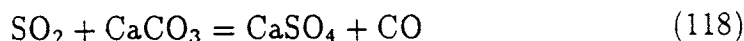


which are suggested to take place in the lower atmosphere close to and at the Venusian surface. Depending on the availability of the required solar uv photons below the clouds and on the reaction rates involved in the photochemical driven disequilibrating reactions and in the thermochemically driven re-equilibrating reactions, these schemes may provide an explanation for the low abundance of COS in the Venusian atmosphere (von Zahn *et al* 1983; Volkov 1986). However, at present this has not been demonstrated quantitatively, and the problem of why the observed COS abundance is significantly lower than the thermochemical equilibrium value remains unsolved.

2.3.7 Sulfur Dioxide and Sulfate Formation on Venus

Likewise, the observed SO_2 mixing ratio also presents a problem because chemical equilibrium models of gas-solid reactions predict that the SO_2 abundance in the lower atmosphere of Venus should be significantly lower than the observed value and should also be less than the abundances of COS and H_2S (Lewis 1968a, 1970a; Lewis and Kreimendahl 1980; Zolotov 1985).

At chemical equilibrium, the SO_2 abundance in the lower Venusian atmosphere will be controlled by gas-solid reactions such as



which have the equilibrium constants

$$\log_{10} K_{118} = -1.82 + 2092(\pm 230)/T \quad (122)$$

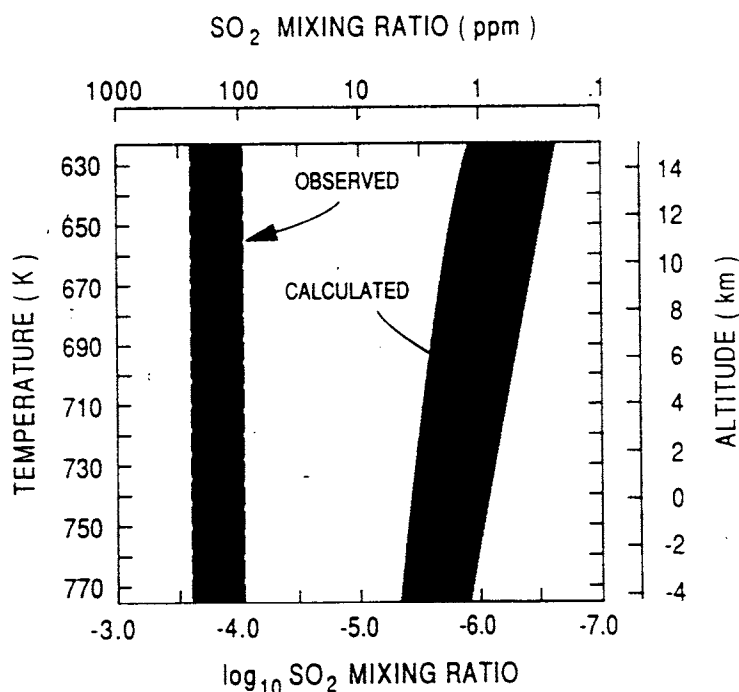


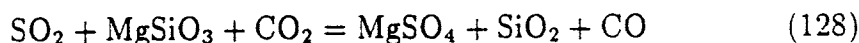
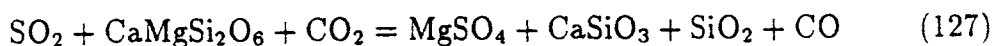
Figure 12. A comparison of the observed and calculated SO_2 mixing ratios in the atmosphere of Venus. The SO_2 mixing ratios observed at 22 km by the Pioneer Venus and the Venera 11/12 gas chromatograph experiments are 185 ± 43 ppm and 130 ± 35 ppm, respectively. In contrast, the SO_2 mixing ratios predicted from equilibrium with calcite CaCO_3 and anhydrite CaSO_4 on the Venus surface are less than 10 ppm. This dichotomy illustrates that sulfur gases in the atmosphere of Venus are not in equilibrium with the surface of Venus.

$$\log_{10}K_{119} = -9.79 + 6548(\pm 229)/T \quad (123)$$

$$\log_{10}K_{120} = -9.55 + 5105(\pm 533)/T \quad (124)$$

$$\log_{10}K_{121} = -11.09 + 6411(\pm 259)/T. \quad (125)$$

As Figure 12 illustrates, the equilibrium SO₂ pressure for reaction (118) is significantly lower than the observed value from the Pioneer Venus (Oyama *et al* 1980) and the Venera 11/12 spacecraft (Gel'man *et al* 1979). However, analogous reactions, such as



which form MgSO₄, are predicted to be unimportant on Venus. This is easily seen by using the equilibrium constants

$$\log_{10}K_{126} = -19.77 + 4980(\pm 2186)/T \quad (129)$$

$$\log_{10}K_{127} = -9.53 + 623(\pm 1194)/T \quad (130)$$

$$\log_{10}K_{128} = -9.77 + 2065(\pm 1095)/T \quad (131)$$

to calculate the equilibrium SO₂ partial pressures. In some cases, such as reaction (126), the equilibrium SO₂ partial pressure at Venus surface conditions (740 K) is ~70 bars, almost the same as the observed CO₂ pressure, while in other cases, such as reactions (127) and (128), the equilibrium P_{SO₂} values are greater than the total atmospheric pressure on Venus. These results demonstrate that MgSO₄ is unstable on the surface of Venus. Likewise, thermochemical data (DeKock 1986) for sulfates of other abundant rock-forming elements (Fe, Al, Na, K, etc.) show that these sulfates are also unstable on the surface of Venus. Thus at chemical equilibrium the SO₂ pressure will be regulated by anhydrite formation. But then how can the observed SO₂ pressure, which is approximately 100 times larger than the equilibrium value produced by reaction (118) be explained?

2.3.8 Kinetics of Anhydrite Formation on Venus

The most plausible explanation is that the reaction of SO₂ with Ca-bearing minerals on the surface of Venus is a slow reaction that does not reach chemical equilibrium. This was suggested by von Zahn *et al* (1983) after the Pioneer Venus and Venera 11/12 missions and was confirmed by the experimental results of Fegley and colleagues (Fegley 1987, 1988, 1990; Fegley and Prinn 1989).

These experiments measured the rate of reaction (118) as a function of temperature in the range 873–1123 K by heating high purity natural calcite crystals of known weight and surface area in CO₂–SO₂ gas mixtures at ~1 atmosphere pressure. The gas mixtures nominally contained 1% SO₂ by volume and thus had a SO₂ molecular number density about the same as that at the surface of Venus. The gas mixtures also typically contained <1 ppm

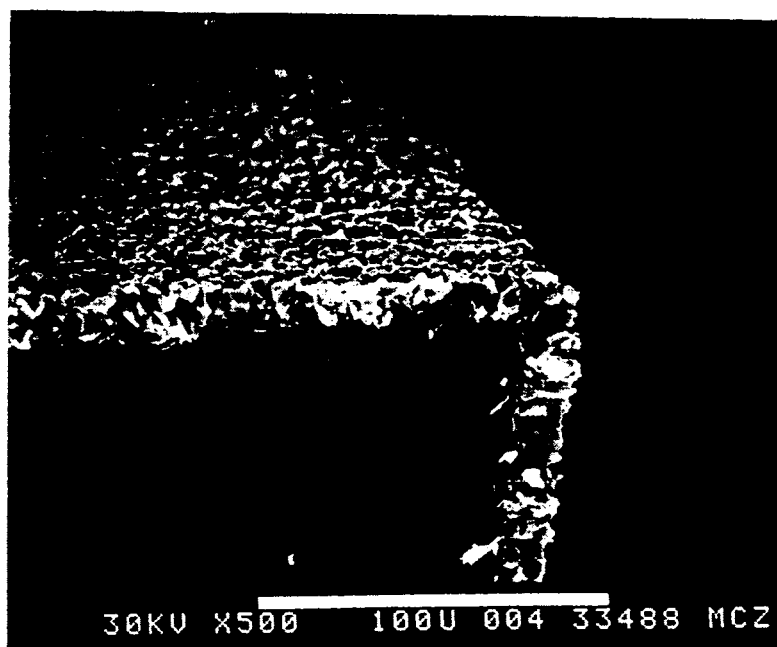


Figure 13. A scanning electron micrograph of the fracture surface of a calcite crystal which has partially reacted with a gas mixture having the nominal composition 1% SO₂ + 99% CO₂. The outer surfaces of the crystal are coated with anhydrite CaSO₄. The reaction conditions were 850°C for 192 hours. The scale bar is 100 μm long. Photo from Fegley and Prinn (1989).

O₂ and ≤10 ppm H₂O as impurities, but experiments done with gas mixtures containing up to 100 ppm O₂ showed that the rates were independent of the f_{O₂} within this range (Fegley and Prinn 1989). We also note that the water vapor content of the experimental gas mixtures is similar to the water vapor mixing ratio at the Venus surface [~20 ppm derived by Moroz *et al* (1979, 1980, 1983) and 10±4 ppm calculated by Lewis and Grinspoon (1990)]. The experimental rate equation (Fegley and Prinn 1989) is

$$R = 10^{19.64(\pm 0.28)} \exp[-15,248(\pm 2970)]/T \quad (132)$$

which has units of SO₂ molecules cm⁻²sec⁻¹. By taking into account the surface area distribution as a function of altitude on Venus, it is possible to derive the global mean rate of CaSO₄ formation from reaction (118) on Venus. This rate is ~ 4.6 × 10¹⁰ molecules cm⁻²sec⁻¹, which is equivalent to ~ 1 μm of CaSO₄ being deposited per year. As Figure 13 illustrates, the thickness of the CaSO₄ layers produced in the laboratory experiments is ~ 15 μm, equivalent to ~15 years of chemical weathering on the surface of Venus. Presumably aeolian weathering (Marshall *et al* 1988) will remove the thin CaSO₄ layers on shorter timescales, so the laboratory rate data are applicable to Venus. Furthermore, we also note that the S/Ca ratios measured by the Venera 13, 14, and Vega 2 spacecraft are less than that expected if all Ca were combined in CaSO₄ (e.g., see Fig. III.106 in Zolotov and Khodakovsky 1989). Thus, at present the surface of Venus is still a net sink for SO₂ loss via anhydrite formation.



Figure 14. A scanning electron micrograph of an external surface of a natural diopside crystal which has partially reacted with a gas mixture having the nominal composition 1% SO_2 + 99% CO_2 . The surface is partially covered with platelets of CaSO_4 , presumed to be anhydrite, surrounded by silicate material, presumed to be unreacted diopside + the thermodynamically stable reaction products silica + enstatite. The reaction conditions were 833°C for 48 hours. The scale bar is 50 μm long. Photo from Fegley and Prinn (1989).

Unpublished laboratory experiments, that were briefly mentioned in Fegley and Prinn (1989), also show that the reaction of SO_2 with diopside, which is predicted thermodynamically to occur via reaction (120), is slower than the analogous reaction of SO_2 with calcite. As illustrated in Figure 14, a natural diopside crystal reacted under conditions similar to those experienced by the calcite crystal shown in Figure 13 has undergone much less conversion to anhydrite.

What do these kinetic data imply for the attainment of chemical equilibrium between SO_2 and Ca-bearing minerals on the surface of Venus? The rate of the reaction between SO_2 + CaCO_3 , which is faster than the reaction between SO_2 + diopside, is still so slow that ~ 1.9 Ma are required to reduce the observed SO_2 pressure in the Venusian atmosphere to the equilibrium partial pressure which is $\sim 1\%$ of the observed value. Thus, reaction (118) is incapable of buffering variations in the SO_2 pressure in the Venusian atmosphere.

2.3.9 Implications for Venus Volcanism

Instead, as discussed by Fegley and Prinn (1989), SO_2 on Venus is apparently in steady state because the constant removal of SO_2 from the atmosphere by reaction with CaCO_3 and other Ca-bearing minerals on the surface of Venus would otherwise drain all SO_2 from the atmosphere on a geologically short

timescale. This would lead to the disappearance of the H_2SO_4 droplet clouds, that are produced by the photochemical oxidation of atmospheric SO_2 . Thus, a source is needed to replace the SO_2 lost by anhydrite formation.

The most plausible source is volcanism, which has occurred on Venus in the past (e.g., Basilevsky and Head 1988) and which may have caused the increased SO_2 levels that were observed by the Pioneer Venus orbiter (Esposito 1984; Esposito *et al* 1988). The volcanism rate that is needed to balance the rate of SO_2 depletion from the Venusian atmosphere is a function of the sulfur content of the erupted material (gas + magma) and the degassing efficiency of the erupted material. This efficiency is close to 100% as indicated by experiments on the rate of pyrite oxidation (Fegley and Treiman 1990) and experiments on the rate of pyrrhotite oxidation (Treiman and Fegley 1991). Assuming that the rate of SO_2 depletion from the Venusian atmosphere is given by the rate of reaction (118) and using different geochemical models for the composition of the erupted material, Fegley and Prinn (1989) estimated that the rate of volcanism on Venus is currently in the range of $0.4\text{--}11 \text{ km}^3 \text{ yr}^{-1}$. In particular, assuming that the erupted material has the mean composition from the Venera 13, 14, and Vega 2 analyses of the Venus surface, the rate of volcanism is $\sim 1 \text{ km}^3 \text{ yr}^{-1}$.

This geochemically estimated rate is in good agreement with several geophysical estimates (Grimm and Solomon 1987; Spohn 1990). It is also similar to the generally quoted rate of $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ for subaerial volcanism on the Earth (Sapper 1929 quoted in Ivanov and Freney 1983) and to the rate of $\sim 20 \text{ km}^3 \text{ yr}^{-1}$ for mid-ocean ridge formation on the Earth (Parsons 1981). Assuming that the present rate of volcanism on Venus is indeed similar to or slightly less than that on the Earth qualitatively suggests that the reaction of SO_2 with calcite controls the rate of SO_2 depletion from the Venusian atmosphere and also implies that calcite is an abundant mineral on the Venus surface. If calcite were totally absent, and the SO_2 depletion rate were controlled by the slower reaction with diopside (which is presumably more representative of SO_2 reactions with Ca-bearing silicates), the volcanism rate on Venus would be much lower than suggested by the independent geophysical estimates and would also be much lower than the terrestrial volcanism rates.

Likewise, the significantly higher geophysical estimates of $\sim 200\text{--}300 \text{ km}^3 \text{ yr}^{-1}$ for Venus volcanism (Solomon and Head 1982; Turcotte 1989) can confidently be ruled out on the basis of the laboratory measurements of SO_2 reaction rates because no reaction is rapid enough to keep pace with the large SO_2 injection rates implied by these much larger volcanism rates. As a consequence, the SO_2 concentration in the Venusian atmosphere would be rapidly increasing with time, contrary to the limited observational evidence which is consistent with a time independent SO_2 mixing ratio below the clouds and a time dependent decrease in the SO_2 mixing ratio above the clouds.

2.4 Hydrogen Halides and Halogen-Bearing Minerals

2.4.1 Atmospheric Abundances of HCl and HF

HCl and HF were discovered in the atmosphere of Venus by Connes *et al* (1967) using high resolution Fourier transform infrared spectroscopy. They found 0.6 ± 0.12 ppm HCl and $5^{+5}_{-2.5}$ ppb HF at the ~ 100 mb level of the atmosphere (i.e., at the cloud tops). A re-analysis of the Connes *et al* data by Young (1972) gave a slightly lower HCl mixing ratio of 0.4 ppm and a slightly higher HF mixing ratio of 10 ppb. However, the only other spectroscopic measurements of HCl and HF on Venus are the observations of DeBergh *et al* (1989) at $3.6\text{--}3.9\ \mu\text{m}$ which found ~ 0.4 ppm HCl at the ~ 35 mb level and the observations of Bézard *et al* (1990) at $2.3\ \mu\text{m}$ of the night side of Venus which found ~ 0.5 ppm HCl and ~ 4.5 ppb HF in the 35 to 45 km region below the clouds.

Although HCl and HF are trace constituents in the atmosphere of Venus, their abundances are orders of magnitude greater than in the terrestrial atmosphere. Taking an HCl mixing ratio of 0.5 ppm the corresponding column density on Venus is $\sim 7 \times 10^{20}$ HCl molecules cm^{-2} . In contrast, the total Cl column density ($\text{HCl} + \text{CH}_3\text{Cl} + 2\text{CF}_2\text{Cl}_2 + 3\text{CFCl}_3 + 3\text{CH}_3\text{CCl}_3 + 4\text{CCl}_4$) in the nonurban terrestrial troposphere is $\sim 6 \times 10^{16}$ Cl atoms cm^{-2} [a mixing ratio of ~ 3.6 ppb total Cl (Prinn and Fegley 1987)]. Likewise, the HF mixing ratio of 5 ppb on Venus corresponds to $\sim 7 \times 10^{18}$ HF molecules cm^{-2} versus a total F column density ($2\text{CF}_2\text{Cl}_2 + \text{CFCl}_3 + 4\text{CF}_4 + \text{HF}$) in the nonurban terrestrial troposphere of $\sim 4 \times 10^{16}$ F atoms cm^{-2} [a mixing ratio of ~ 2.1 ppb total F (Prinn and Fegley 1987)].

Thus, HCl on Venus is $\sim 10,000$ times more abundant than total atmospheric Cl on Earth. Furthermore, about 70% of the total Cl in the terrestrial atmosphere is in man-made compounds such as the chlorofluorocarbon gases and CCl_4 , while the remaining 30% (HCl) is produced from sea salt sprayed into the atmosphere. Likewise, HF on Venus is ~ 200 times more abundant than total atmospheric F on Earth, which is almost totally due to man-made compounds such as the chlorofluorocarbons and CF_4 . However, the atmospheric abundances of HCl and HF on Venus are a direct reflection of the high surface temperature of Venus.

2.4.2 Origin of Atmospheric HCl and HF on Venus

Shortly after the discovery of HCl and HF on Venus, Lewis (1968a, 1970a) and Mueller (1968, 1969) proposed that the atmospheric abundances of HCl and HF are buffered by chemical equilibria between halogen-bearing minerals and other silicates on the surface of Venus. The corrosive nature of both HCl and HF intuitively suggests that this explanation is reasonable. Furthermore, the essentially identical values observed for both HCl and HF by Connes *et al* (1967) above the clouds and by Bézard *et al* (1990) below the clouds suggests that the abundances of these two gases are not controlled by episodic phenomena such as volcanic eruptions but instead reflect equilibrium values. Finally, a calculation of the Cl/C and F/C atomic ratios on the Earth's

Table 10. Possible HCl Buffers on Venus (Lewis, 1970a)

9.1	$2\text{HCl} + \text{CaSiO}_3 + 2\text{NaAlSiO}_4 = 2\text{NaCl} + \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SiO}_2 + \text{H}_2\text{O}$ wollastonite + nepheline + halite + anorthite + quartz $\log_{10}K_{9.1} = -6.45 + 10231(\pm 271)/T$ $X_{\text{HCl}} \sim 9 \times 10^{-8}$
9.2	$2\text{HCl} + 2\text{NaAlSi}_3\text{O}_8 = 2\text{NaCl} + \text{Al}_2\text{SiO}_5 + 5\text{SiO}_2 + \text{H}_2\text{O}$ analbite + halite + andalusite + quartz $\log_{10}K_{9.2} = -9.20 + 8723(\pm 490)/T$ $X_{\text{HCl}} \sim 2 \times 10^{-5}$
9.3	$2\text{HCl} + 2\text{NaAlSi}_2\text{O}_6 = 2\text{NaCl} + \text{Al}_2\text{SiO}_5 + 3\text{SiO}_2 + \text{H}_2\text{O}$ jadeite + halite + andalusite + quartz $\log_{10}K_{9.3} = -3.97 + 7138(\pm 488)/T$ $X_{\text{HCl}} \sim 7 \times 10^{-7}$
9.4	$2\text{HCl} + 2\text{NaAlSi}_3\text{O}_8 + 6\text{NaAlSiO}_4 = \text{Al}_2\text{SiO}_5 + 2\text{Na}_4[\text{AlSiO}_4]_3\text{Cl} + 5\text{SiO}_2 + \text{H}_2\text{O}$ analbite + nepheline + andalusite + sodalite + quartz $\log_{10}K_{9.4} = -15.75 + 14347(\pm 2137)/T$ $X_{\text{HCl}} \sim 9 \times 10^{-14}$
9.5	$2\text{HCl} + 8\text{NaAlSiO}_4 = 2\text{Na}_4[\text{AlSiO}_4]_3\text{Cl} + \text{Al}_2\text{SiO}_5 + \text{SiO}_2 + \text{H}_2\text{O}$ nepheline + sodalite + andalusite + quartz $\log_{10}K_{9.5} = -14.31 + 15718(\pm 2191)/T$ $X_{\text{HCl}} \sim 2 \times 10^{-7}$
9.6	$6\text{HCl} + 2\text{Na}_4[\text{AlSiO}_4]_3\text{Cl} + 3\text{CaSiO}_3 = 8\text{NaCl} + 3\text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{SiO}_2 + 3\text{H}_2\text{O}$ sodalite + wollastonite + halite + anorthite + quartz $\log_{10}K_{9.6} = -12.80 + 25070(\pm 1951)/T$ $X_{\text{HCl}} \sim 2 \times 10^{-17}$

surface [oceans + sediments + crust values from Smith (1981) and Ronov and Yaroshevsky (1976)] shows that both the Cl/C ratio of ~ 0.12 and the F/C ratio of ~ 0.09 are significantly greater than the Venusian atmospheric Cl/C and F/C atomic ratios. Cosmochemical models predict similar Cl and F inventories for both Venus and Earth (Fegley and Lewis, 1980). Thus, this comparison suggests that the HCl and HF abundances in the atmosphere of Venus do not represent the total inventories of Cl and F for the planet and that significant amounts of Cl and F are still present on the surface of Venus.

2.4.3 HCl Reactions with Cl-Bearing Minerals

Gas-solid reactions that might buffer the HCl pressure in the Venusian atmosphere were first considered in detail by Lewis (1970a). His reactions along with linear fits to the equilibrium constants in the 600 to 800 K range are listed in Table 10. The equilibrium constants were calculated using thermodynamic data from Robie *et al* (1979), Hemingway *et al* (1982), and Sharp *et al* (1989), who give thermodynamic data for sodalite. Lewis (1970a) used the sodalite data of Wellman (1969) in his calculations; however, the Sharp *et al* (1989) data are more accurate and are preferred. The equilibrium HCl mixing ratios at 740 K and 20 ppm H_2O are also listed in Table 10. Inspection of the equilibrium constant expressions for the reactions in Table 10 shows that

$$X_{\text{HCl}} \propto X_{\text{H}_2\text{O}}^{\frac{1}{2}} \quad (133)$$

for reactions (1)–(5) and that

$$X_{\text{HCl}} \propto X_{\text{H}_2\text{O}}^{\frac{3}{2}} \quad (134)$$

for reaction (6). Thus, if 100 ppm H₂O were used instead, the calculated HCl mixing ratios would be only $\sqrt{5}$ times larger for reactions (1)–(5) and ~ 11 times larger for reaction (6). However, it is unlikely that the water vapor mixing ratio at the surface of Venus is this large.

Of the buffers originally proposed by Lewis (1970a), only reaction (2) represents a stable equilibrium. However, this reaction is not an appropriate HCl buffer for the Venusian atmosphere because the equilibrium HCl mixing ratio is ~ 40 times larger than the observed value. The discrepancy between the equilibrium predictions and the observations is too large to be attributed to the uncertainties in the thermodynamic data and in the HCl observations.

Orville (1974) noted that reactions (1) and (3), which were the buffers favored by Lewis (1970a), cannot be stable equilibria anywhere on the surface of Venus. Reaction (1) involves nepheline + quartz which are unstable relative to albite. Reaction (3) involves jadeite, which is unstable below ~ 10 kilobars pressure. We also note that reactions (4)–(6) cannot be stable equilibria. They all involve the assemblage sodalite + quartz which is metastable with respect to albite + halite or with respect to marialite-bearing assemblages. Furthermore, reactions (4) and (5) also include nepheline + andalusite, which are metastable with respect to albite + corundum.

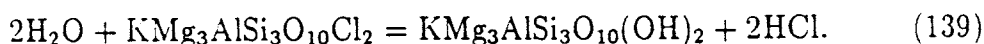
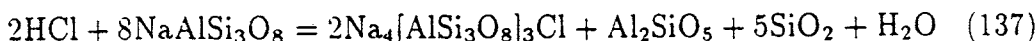
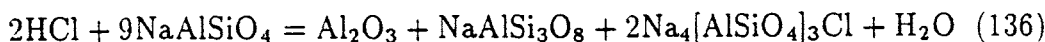
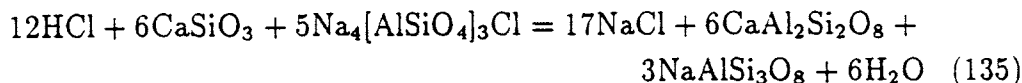
We emphasize that these objections, which are based on well known phase equilibria determined by experimental petrology, rule out the HCl buffers proposed by Lewis (1970a). The agreement between the calculated and observed HCl mixing ratios for reactions (1) and (3), which has been cited by several authors (e.g., Prinn 1985; von Zahn *et al* 1983) as evidence that these reactions are buffering HCl in the Venusian atmosphere, is merely a coincidence.

Lewis (1970a) also proposed that nepheline is absent from the surface of Venus because otherwise HCl would react to form sodalite and thus be removed from the atmosphere. In this regard we note that nepheline is the most characteristic mineral of terrestrial alkaline rocks and occurs as a primary phase in many volcanic rocks with different mineralogical and chemical compositions (Deer *et al* 1963). We also point out that the Venera 8 and 13 sites have been interpreted as high-potassium alkaline basalts and that the calculated normative composition at the Venera 13 site includes 8% nepheline (Volkov *et al* 1986). By analogy with the Earth, we feel that it is unlikely that nepheline is absent from the surface of Venus.

Lewis' conclusion was based on very low HCl pressures calculated for reactions involving sodalite. However, in some cases the low HCl pressures are simply a reflection of the incorrect sodalite data from Wellman (1969). Sharp *et al* (1989) show that Wellman's (1969) data are based on a metastable equilibrium and find that sodalite is in fact less stable than Wellman's data indicate. The difference is substantial; for reaction (5) Wellman's sodalite data yield $X_{\text{HCl}} \sim 3 \times 10^{-13}$ versus $\sim 2 \times 10^{-7}$ as shown in Table 10. As noted above, reactions (4)–(6) cannot be stable equilibria. Thus, we interpret the

very low HCl pressures calculated for some sodalite reactions as showing that the non-equilibrium mineral assemblages involved are not found on the surface of Venus.

Taking into account stable phase equilibria and using terrestrial petrology as a guide, we propose five other buffering reactions for HCl on Venus. These reactions are



The equilibrium constants for reactions (135)–(138) were calculated from thermodynamic data in Robie *et al* (1979), Hemingway *et al* (1982), Sharp *et al* (1989), Semenov *et al* (1981), and Zhu and Sverjensky (1990) and are given by the equations

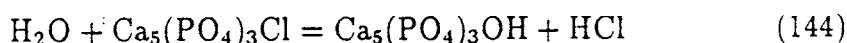
$$\log_{10}K_{135} = -20.17 + 49384(\pm 4884)/T \quad (140)$$

$$\log_{10}K_{136} = -13.56 + 16150(\pm 2259)/T \quad (141)$$

$$\log_{10}K_{137} = -14.92 + 15143(\pm 1566)/T \quad (142)$$

$$\log_{10}K_{138} = 0.06 + 2837(\pm 845)/T \quad (143)$$

from 600 to 800 K. Another potential HCl buffer is analogous to reaction (138):



but the equilibrium constant given by data from Zhu and Sverjensky (1990)

$$\log_{10}K_{144} = -0.16 - 2283(\pm 496)/T \quad (145)$$

indicates that coexisting hydroxy-apatite and chlor-apatite present anywhere on the surface of Venus will yield HCl mixing ratios below the observed value (e.g., 0.002 to 0.05 ppm HCl for buffering at 740 K). This result along with the ability of reaction (138) to provide the required amounts of HCl from buffering by a solid solution of fluor- and chlor-apatite, suggests that hydroxy-apatite is absent from the surface of Venus.

The equilibrium constant for reaction (139) cannot be calculated because no thermodynamic data are available for chlor-phlogopite. This reaction is proposed as a potential HCl buffer on Venus because chlorine is a common, if minor, constituent of micas such as phlogopite on the Earth.

However, our preferred HCl buffers are reactions (135) and (136). As shown in Tables 11 and 12, within the uncertainties of the thermodynamic

Table 11. Equilibrium Abundances of HCl Buffered by Sodalite + Albite

Altitude (km)	Temperature (K)	HCl Mixing Ratios and the Range of Values
-4	770	0.44 ppm (0.13 ppm - 1.48 ppm)
-2	755	0.35 ppm (0.10 ppm - 1.21 ppm)
0	740	0.28 ppm (0.08 ppm - 0.98 ppm)
2	725	0.22 ppm (0.06 ppm - 0.79 ppm)
4	710	0.17 ppm (0.04 ppm - 0.63 ppm)
6	695	0.13 ppm (0.03 ppm - 0.49 ppm)
8	679	0.10 ppm (0.02 ppm - 0.38 ppm)
10	663	0.07 ppm (0.02 ppm - 0.29 ppm)
12	648	0.05 ppm (0.01 ppm - 0.22 ppm)

Table 12. Equilibrium Abundances of HCl Buffered by Sodalite + Nepheline

Altitude (km)	Temperature (K)	HCl Mixing Ratios and the Range of Values
-4	770	81 ppb (2.8 ppb - 2370 ppb)
-2	755	53 ppb (1.7 ppb - 1660 ppb)
0	740	34 ppb (1.0 ppb - 1140 ppb)
2	725	21 ppb (0.6 ppb - 770 ppb)
4	710	13 ppb (0.3 ppb - 520 ppb)
6	695	8.1 ppb (0.2 ppb - 340 ppb)
8	679	4.6 ppb (0.1 ppb - 210 ppb)
10	663	2.5 ppb (0.05 ppb - 130 ppb)
12	648	1.4 ppb (0.03 ppb - 80 ppb)

data, both buffers provide the required amounts of HCl with reaction (135) giving a closer match to the observed HCl mixing ratio. If reaction (135) is responsible for buffering HCl in the Venusian atmosphere then halite is stable on the Venusian surface. The lower HCl equilibrium mixing ratios resulting from reaction (136) cannot be used to argue that the assemblage sodalite + albite + nepheline is absent from the surface of Venus because within the uncertainties of the thermodynamic data, the equilibrium HCl mixing ratio matches the observed value. In fact, the mineral assemblage sodalite + nepheline \pm albite is common in terrestrial nepheline-syenites (Deer *et al* 1963) and by analogy with the Earth would also be expected on Venus as well.

Reaction (137) involving the scapolite marialite is also a possible buffer for HCl on Venus. Using equation (142) calculated with the marialite data of Semenov *et al* (1981), we find that at 740 K the equilibrium HCl mixing ratio is ~ 0.8 ppm. The uncertainty in the thermodynamic data allow a range of HCl mixing ratios from ~ 0.07 ppm to ~ 9 ppm at this temperature. Thus, reaction (137) may also be a viable HCl buffer. However, as noted previously in section (2.1.3), marialite may not be as stable as the Semenov *et al* data predict and thus reaction (137) may not be important for Venus. Further studies of the thermodynamic properties of well characterized marialite samples are required to resolve this issue.

Table 13. Possible HF Buffers on Venus (Lewis, 1970a)

10.1	$2\text{HF} + \text{CaSiO}_3 = \text{CaF}_2 + \text{SiO}_2 + \text{H}_2\text{O}$ wollastonite + fluorite + quartz $\log_{10}K_{10.1} = -6.53 + 10432(\pm 109)/T$ $X_{\text{HF}} \sim 8 \times 10^{-8}$
10.2	$4\text{HF} + \text{Ca}_2\text{MgSi}_2\text{O}_7 = 2\text{CaF}_2 + \text{SiO}_2 + \text{MgSiO}_3 + 2\text{H}_2\text{O}$ åkermanite + fluorite + quartz + enstatite $\log_{10}K_{10.2} = -14.12 + 22415(\pm 244)/T$ $X_{\text{HF}} \sim 4 \times 10^{-8}$
10.3	$2\text{HF} + \text{CaMgSiO}_4 = \text{CaF}_2 + \text{MgSiO}_3 + \text{H}_2\text{O}$ monticellite + fluorite + enstatite $\log_{10}K_{10.3} = -6.82 + 10988(\pm 215)/T$ $X_{\text{HF}} \sim 4 \times 10^{-8}$
10.4	$2\text{HF} + \text{MgSiO}_3 = \text{MgF}_2 + \text{SiO}_2 + \text{H}_2\text{O}$ enstatite + sellaite + quartz $\log_{10}K_{10.4} = -6.40 + 9464(\pm 135)/T$ $X_{\text{HF}} \sim 3 \times 10^{-7}$
10.5	$2\text{HF} + \text{Mg}_2\text{SiO}_4 = \text{MgF}_2 + \text{MgSiO}_3 + \text{H}_2\text{O}$ forsterite + sellaite + enstatite $\log_{10}K_{10.5} = -6.64 + 10314(\pm 141)/T$ $X_{\text{HF}} \sim 1 \times 10^{-7}$
10.6	$6\text{HF} + 2\text{CaSiO}_3 + 3\text{NaAlSi}_3\text{O}_8 = \text{Na}_3\text{AlF}_6 + 10\text{SiO}_2 + \text{Ca}_2\text{Al}_2\text{SiO}_7 + 3\text{H}_2\text{O}$ wollastonite + analbite + cryolite + quartz + gehlenite $\log_{10}K_{10.6} = -22.84 + 22877(\pm 894)/T$ $X_{\text{HF}} \sim 2 \times 10^{-5}$
10.7	$2\text{HF} + \text{KAlSi}_2\text{O}_6 + 3\text{MgSiO}_3 = \text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2 + 2\text{SiO}_2 + \text{H}_2\text{O}$ leucite + enstatite + fluorphlogopite + quartz $\log_{10}K_{10.7} = -8.24 + 12250(\pm 1841)/T$ $X_{\text{HF}} \sim 3 \times 10^{-8}$
10.8	$2\text{HF} + \text{KAlSi}_3\text{O}_8 + 3\text{MgSiO}_3 = \text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2 + 3\text{SiO}_2 + \text{H}_2\text{O}$ sanidine + enstatite + fluorphlogopite + quartz $\log_{10}K_{10.8} = -6.61 + 11236(\pm 1848)/T$ $X_{\text{HF}} \sim 2 \times 10^{-8}$
10.9	$2\text{HF} + \text{KAlSi}_2\text{O}_6 + 2\text{Mg}_2\text{SiO}_4 = \text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2 + \text{MgSiO}_3 + \text{H}_2\text{O}$ leucite + forsterite + fluorphlogopite + enstatite $\log_{10}K_{10.9} = -8.71 + 13948(\pm 1834)/T$ $X_{\text{HF}} \sim 4 \times 10^{-9}$

2.4.4 HF Reactions with F-Bearing Minerals

Lewis (1970a) also considered a number of gas-solid reactions as possible HF buffers on Venus. These are listed in Table 13 along with linear fits to the equilibrium constants in the 600 to 800 K range. The fits were calculated using thermodynamic data from Robie *et al* (1979), Hemingway *et al* (1982), and the JANAF Tables (Chase *et al* 1985). The equilibrium HF mixing ratios in Table 13 are calculated at 740 K for 20 ppm H_2O . However, like several of the HCl buffers in Table 10, the HF mixing ratio is proportional to $X_{\text{H}_2\text{O}}^{1/2}$.

Of the reactions listed in Table 13, only a few yield equilibrium HF mixing ratios low enough to match or come close to the observed value. Lewis (1970a) originally suggested reaction (2) in Table 13 as the HF buffering reaction on Venus. However, Orville (1974) noted that åkermanite, which is involved in reaction (2), is thermodynamically unstable at CO_2 pressures above

Table 14. Equilibrium Abundances of HF Buffered by Fluorphlogopite in Felsic Rocks

Altitude (km)	Temperature (K)	HF Mixing Ratios and the Range of Values
-4	770	24 ppb (1.5 ppb - 390 ppb)
-2	755	19 ppb (1.1 ppb - 320 ppb)
0	740	14 ppb (0.8 ppb - 250 ppb)
2	725	11 ppb (0.6 ppb - 200 ppb)
4	710	8 ppb (0.4 ppb - 160 ppb)
6	695	6 ppb (0.3 ppb - 120 ppb)
8	679	4 ppb (0.2 ppb - 90 ppb)
10	663	3 ppb (0.1 ppb - 70 ppb)
12	648	2 ppb (.07 ppb - 50 ppb)

~0.1 bars and will react to form diopside + calcite. Thus, the åkermanite + fluorite + quartz + enstatite assemblage in reaction (2) cannot exist on the Venusian surface. The agreement between the calculated HF mixing ratio for this reaction and the observed value, which has been cited by several authors (e.g., Prinn 1985; von Zahn *et al* 1983) as evidence that reaction (2) is buffering HF on Venus, is again only a coincidence.

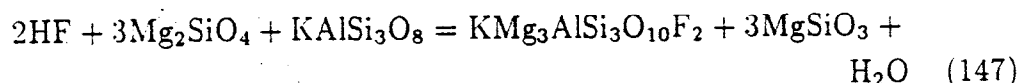
Likewise, several of the other HF buffers suggested by Lewis (1970a) involve mineral assemblages known to be unstable or metastable. Reaction (7) involves leucite + quartz which reacts to form K-feldspar and reaction (9) involves leucite + enstatite which reacts to form K-feldspar + olivine. Neither reaction can be considered as a HF buffer because the mineral assemblages involved will not exist at equilibrium on the surface of Venus.

Only reaction (8), which is the stability limit for fluor-phlogopite in felsic (i.e., granitic) rocks, may be a viable HF buffer. However, at Venusian surface temperatures, K-feldspar is probably totally ordered (Ribbe 1983; Yund and Tullis 1983) and thus microcline should be used instead of sanidine (as done by Lewis) in this reaction. This changes the equilibrium constant to

$$\log_{10}K_8 = -5.53 + 10765(\pm 1848)/T \quad (146)$$

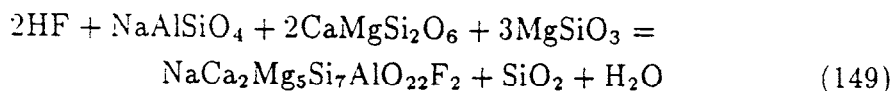
and the equilibrium HF mixing ratio at 740 K to $\sim 1 \times 10^{-8}$. As shown in Table 14, within the uncertainties of the thermodynamic data, this reaction is a viable HF buffer on Venus.

Again taking into account stable phase equilibria and using terrestrial petrology as a guide, we propose three additional gas-solid reactions as HF buffers on Venus. These reactions and the corresponding equilibrium constants calculated from thermodynamic data in Robie *et al* (1979) and Graham and Navrotsky (1986) are



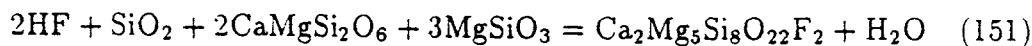
$$\log_{10}K_{147} = -6.23 + 13313(\pm 1852)/T \quad (148)$$

involving the mineral assemblage forsterite + microcline + fluor-phlogopite + enstatite which governs the stability of fluor-phlogopite in mafic (i.e., basaltic) rocks,



$$\log_{10}K_{149} = -6.88 + 12098(\pm 1120)/T \quad (150)$$

involving the mineral assemblage nepheline + diopside + enstatite + fluor-edenite + quartz, and



$$\log_{10}K_{151} = -7.39 + 11113(\pm 1223)/T \quad (152)$$

involving the mineral assemblage quartz + diopside + enstatite + fluor-tremolite.

The calculated equilibrium HF mixing ratios as a function of altitude for these reactions are listed in Tables 15-17. The equilibrium HF mixing ratios

Table 15. Equilibrium Abundances of HF Buffered by Fluorphlogopite in Mafic Rocks

Altitude (km)	Temperature (K)	HF Mixing Ratios and the Range of Values		
-4	770	1 ppb	(0.08 ppb	- 19 ppb)
-2	755	0.9 ppb	(0.05 ppb	- 15 ppb)
0	740	0.6 ppb	(0.03 ppb	- 11 ppb)
2	725	0.4 ppb	(0.02 ppb	- 8 ppb)
4	710	0.3 ppb	(0.01 ppb	- 6 ppb)
6	695	0.2 ppb	(.009 ppb	- 4 ppb)
8	679	0.1 ppb	(.005 ppb	- 3 ppb)
10	663	.08 ppb	(.003 ppb	- 2 ppb)
12	648	.05 ppb	(.002 ppb	- 1 ppb)

Table 16. Equilibrium Abundances of HF Buffered by Fluor-Edenite in Mafic Rocks

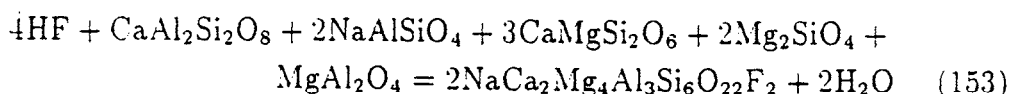
Altitude (km)	Temperature (K)	HF Mixing Ratios and the Range of Values		
-4	770	16 ppb	(3 ppb	- 84 ppb)
-2	755	12 ppb	(2 ppb	- 64 ppb)
0	740	8 ppb	(1.5 ppb	- 48 ppb)
2	725	6 ppb	(1 ppb	- 36 ppb)
4	710	4 ppb	(0.7 ppb	- 27 ppb)
6	695	3 ppb	(0.5 ppb	- 19 ppb)
8	679	2 ppb	(0.3 ppb	- 14 ppb)
10	663	1 ppb	(0.2 ppb	- 9 ppb)
12	648	0.9 ppb	(0.1 ppb	- 6 ppb)

Table 17. Equilibrium Abundances of HF Buffered by Fluor-Tremolite in Felsic Rocks

Altitude (km)	Temperature (K)	HF Mixing Ratios and the Range of Values
-4	770	124 ppb (20 ppb - 770 ppb)
-2	755	94 ppb (15 ppb - 610 ppb)
0	740	70 ppb (10 ppb - 470 ppb)
2	725	52 ppb (8 ppb - 370 ppb)
4	710	39 ppb (5 ppb - 280 ppb)
6	695	28 ppb (4 ppb - 210 ppb)
8	679	19 ppb (2.4 ppb - 150 ppb)
10	663	13 ppb (1.6 ppb - 110 ppb)
12	648	9 ppb (1 ppb - 80 ppb)

for reaction (149) are very close to the observed value; however, within the uncertainties in the thermodynamic data, all three reactions are viable HF buffers over a range of altitudes on the Venusian surface.

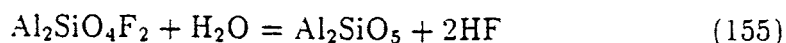
We also examined the stability of fluor-pargasite (a fluor-hornblende) using thermodynamic data from Westrich (1981), Westrich and Navrotsky (1981), and Robie *et al* (1979). The reaction studied and the equilibrium constant in the 600 to 800 K range are



$$\log_{10}K_{153} = -10.22 + 16102(\pm 1918)/T. \quad (154)$$

At 740 K, the HF mixing ratio needed to stabilize fluor-pargasite on the Venusian surface is ~600 ppb, or about 100 times greater than the observed value. At altitudes of ~9 km and above, the uncertainties in the thermodynamic data permit fluor-pargasite to be stable; however, then the kinetics of reaction (153) become an important issue. Experimental studies of reaction (153) could resolve this question and would also be important for assessing fluor-pargasite stability on the Earth.

Another buffer that we examined involved fluor-topaz $\text{Al}_2\text{SiO}_4\text{F}_2$. This reaction is



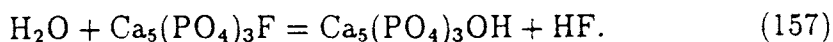
and the equilibrium constant calculated using the fluor-topaz data of Barton *et al* (1982) is

$$\log_{10}K_{155} = 7.65 - 10115(\pm 283)/T. \quad (156)$$

However, reaction (155) is not a viable HF buffer anywhere on the surface of Venus. For example, at 740 K the equilibrium HF mixing ratio is ~450 ppb, approximately 90 times higher than the observed value.

For the sake of completeness, we also studied the HF analog to reaction

(138) above:



The equilibrium constant calculated from data in Zhu and Sverjensky (1990) for the apatites and from Robie *et al* (1979) and the JANAF Tables for the other phases is

$$\log_{10}K_{157} = -0.22 - 5120(\pm 498)/T \quad (158)$$

in the 600 to 800 K range. If both hydroxy-apatite and fluor-apatite are present on the surface of Venus, then HF should be buffered at a mixing ratio of $\sim 1.4 \times 10^{-12}$. This value is appropriate for 740 K, but buffering at both higher and lower altitudes also yields equilibrium HF mixing ratios orders of magnitude lower than the observed value of ~ 5 ppb. This result reinforces our earlier conclusions that hydroxy-apatite is absent from the surface of Venus.

Apatites are common accessory minerals in almost all igneous rocks on the Earth and are the most abundant P-bearing minerals (Deer *et al* 1963). Furthermore, fluor-apatite is by far the most commonly found member of the apatite group. In addition, using the equilibrium constant for reaction (138) and assuming ideal solid solution, we calculate that a solid solution of fluor- and chlor-apatite is stable on the surface of Venus. Thus, we suggest that fluor-apatite solid solutions with chlor-apatite are probably present as an accessory mineral on the Venusian surface, but that hydroxy-apatite is probably absent. In fact, if we assume that fluor-apatite is present on Venus, and calculate the hydroxy-apatite thermodynamic activity for reaction (157) at 740 K, we find that it is $\sim 3 \times 10^{-4}$. This activity is far too low for hydroxy-apatite to be a significant component in solid solution with fluor-apatite, and again demonstrates the difficulty in finding any water-bearing minerals stable under Venusian surface conditions.

In summary, we emphasize that HCl and HF are reactive gases which are likely to be in chemical equilibrium with the surface mineralogy in at least some regions of the surface of Venus. The virtually identical HCl and HF mixing ratios observed 20 years apart in two different regions of the Venusian atmosphere also suggest that the observed abundances are equilibrium values. We suggest that the best way to resolve the questions about which reactions are actually buffering HCl and HF on Venus is to study experimentally the thermodynamics and kinetics of several potential buffering reactions. The most attractive candidates for experimental study of HCl buffers are reactions (135) and (136) which provide the required amounts of HCl and which involve common mineral assemblages in nepheline-syenite rocks on the Earth. The most attractive candidates for experimental study of HF buffers are reactions (147), (149), (151), and reaction (8) in Table 13. The latter reaction was originally suggested by Lewis (1970a). All the HF reactions also involve stable mineral assemblages observed in different rock types on the Earth and their study will thus yield information relevant to terrestrial petrology as well.

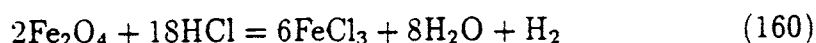
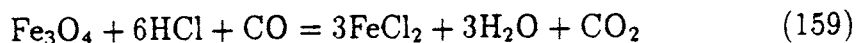
2.4.5 Cl-Bearing Cloud Condensates

Chlorine-bearing cloud particles were apparently detected by several experiments on the Venera 11/12, Venera 13/14, and Vega 1/2 spacecraft. However, these reports have met with considerable skepticism because of the geochemical problems involved in identifying any plausible Cl-bearing condensates that could be present at the required abundance in the cloud-forming region of the Venusian atmosphere. We review this situation by first presenting the observational evidence and then discussing the theoretical arguments involved.

Surkov *et al* (1981) reported that the Venera 11/12 X-ray fluorescence (XRF) experiment detected Cl in the Venusian clouds and reported S/Cl mass ratios of ~ 0.1 . An upper limit of 2% (by mass) was also established for the Cl/Hg mass ratio. Furthermore, Petryanov *et al* (1981) reported that the XRF experiment also detected Fe in the cloud layers. Surkov *et al* (1982) subsequently reported that the XRF experiment on the Venera 13/14 spacecraft measured S/Cl mass ratios of ~ 7 in the Venus clouds. Finally, an X-ray radiometric experiment (Andreichikov *et al* 1987) and a mass spectrometer experiment (Surkov *et al* 1987) on the Vega 1/2 spacecraft also reported the presence of Cl in the clouds. However, none of these experiments provided any information on the putative Cl-bearing compounds present in the cloud layers. What Cl-bearing compounds have been suggested to be present and how plausible are they on theoretical grounds?

One possible Cl-bearing cloud condensate which has been discussed in the literature is HCl (e.g., Lewis 1968a,b, 1969, 1970c, 1971c). However, the presence of HCl solution clouds is inconsistent with observational data on HCl and H₂O abundances, cloud particle refractive indices, and with the Venera 11-14 data (Esposito *et al* 1983; Krasnopolsky 1986). Mercury chlorides were also suggested by Lewis (1969), but neither the Pioneer Venus mass spectrometer (Hoffman *et al* 1980a) nor the Venera 11/12 XRF experiment (Surkov *et al* 1981) has detected any Hg-bearing gases or condensates in the Venusian atmosphere.

Iron chlorides and their hydrates have been discussed by several groups as possible cloud-forming condensates (Kuiper 1969, 1971; Knollenberg and Hunten 1980; Krasnopolsky 1985, 1989; Krasnopolsky and Parshev 1979). However, the problem with this suggestion is that the required abundance of Fe chlorides (a mixing ratio of ~ 10 ppm by volume) is much larger than the equilibrium abundance of FeCl₂ or of FeCl₃ supplied by gas-solid reactions with the surface of Venus. This point was probably first emphasized by Lewis (1970a) who considered the reactions



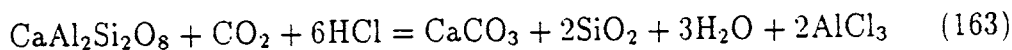
which have the equilibrium constants

$$\log_{10} K_{159} = 8.23 - 11038(\pm 354)/T \quad (161)$$

$$\log_{10} K_{160} = -2.31 - 20544(\pm 1595)/T. \quad (162)$$

At 740 K reaction (159) yields an FeCl_2 mixing ratio of $\sim 10^{-11.7}$ at equilibrium, while reaction (160) yields an even lower FeCl_3 mixing ratio of $\sim 10^{-15.2}$ at equilibrium. The latter calculation assumes that the H_2 partial pressure is fixed by equilibrium with Fe-bearing silicates on the surface of Venus. However, if the significantly higher H_2 mixing ratio of 10 ppm estimated by Kumar *et al* (1981) is used instead, the calculated FeCl_3 mixing ratio decreases to $\sim 10^{-15.8}$. Thus, Fe chlorides are not present at abundances anywhere near those required to explain the reported Cl mass densities.

Aluminum chlorides (AlCl_3 and Al_2Cl_6) have also been suggested by Krasnopolsky and colleagues (Krasnopolsky 1985, 1989; Krasnopolsky and Parshev 1979) to explain the Venera and Vega observations. However, this proposal must also be rejected because the volatility of Al chlorides is too low to provide the necessary Cl mass densities (Lewis and Fegley 1982). They noted that the reaction



which has the equilibrium constant

$$\log_{10} K_{163} = -8.80 - 13056(\pm 165)/T \quad (164)$$

will control the abundance of AlCl_3 gas evolved from felsic rocks on the surface of Venus. At 740 K, the equilibrium mixing ratio of AlCl_3 is only $10^{-23.1}$, which is about 18 orders of magnitude too low to provide the observed cloud condensate mass densities.

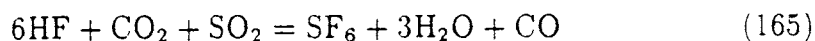
Lewis and Fegley (1982) also critically assessed the plausibility of As and Sb chlorides as cloud-forming condensates. These compounds had previously been suggested by Soviet scientists (e.g., Barsukov *et al* 1981) who calculated that chlorides were the dominant As- and Sb-bearing gases in the atmosphere of Venus and that the mixing ratios of these species were large enough to explain the observed cloud condensate densities. However, using more recent thermodynamic data for a large number of As and Sb gases and condensed phases, Lewis and Fegley (1982) showed that in fact the dominant As- and Sb-bearing gases are sulfides and not chlorides and that in any case the volatility of As and Sb compounds is sufficiently low that they are unable to provide the necessary mass densities.

Thus, exhaustive thermodynamic modelling has so far failed to provide any geochemically plausible mechanism to explain the reported Cl-bearing cloud condensates. In the absence of any other quantitative proposal for explaining these observations, we conclude that the spacecraft results must be regarded as provisional and need to be confirmed independently by other investigators.

2.4.6 Sulfur Hexafluoride

Finally, we will consider the detection of 0.2 ppm SF_6 which was claimed by the Venera 13/14 gas chromatography experiment (Mukhin *et al* 1983). This

result is suspect because the reported SF₆ concentration is orders of magnitude greater than is predicted from thermochemical equilibrium between HF and SO₂. This is easily illustrated by considering the reaction

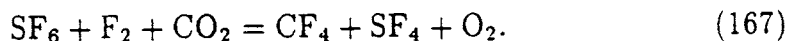


which has the equilibrium constant

$$\log_{10} K_{165} = -23.76 - 13959(\pm 337)/T. \quad (166)$$

Thermochemical equilibrium at the Venusian surface temperature of 740 K yields a SF₆ mixing ratio of $\sim 3 \times 10^{-72}$, while equilibrium at an altitude of ~ 47 km ($T \sim 380$ K), in the middle of the altitude range where SF₆ was reported, yields an even lower mixing ratio of $\sim 2 \times 10^{-95}$. These equilibrium values are approximately 65 to 88 orders of magnitude smaller than the reported mixing ratio of 0.2 ppm.

Zolotov and Khodakovsky (1985) attempted to explain the reported SF₆ abundance by recourse to equilibrium chemistry in putative volcanic gases. Their calculations assumed that the total F atomic abundance in the volcanic gases exceeded the total H atomic abundance thus forcing the excess fluorine to react with sulfur. However, their theoretical results are suspect for the following reasons. First, their assumed fluorine abundance ($F/C \sim 0.001$) is $\sim 2 \times 10^5$ times higher than the observed HF/CO₂ mixing ratio in the Venusian atmosphere. Second, their results predict much larger amounts of CF₄ which has not been observed on Venus. This point is illustrated using their published results and considering the reaction



At 1400 K reaction (167) has an equilibrium constant of $10^{6.05}$. Combining this with their calculated mixing ratios for F₂, CO₂, SF₄, and O₂ displayed in Figure 1 of Zolotov and Khodakovsky (1985), we find that the ratio of the abundances of CF₄ and SF₆ is $\text{CF}_4/\text{SF}_6 \sim 10^{8.4}$, corresponding to ~ 50 ppm CF₄ if the SF₆ abundance is 0.2 ppm as reported by Mukhin *et al* (1983). The arguments outlined in this section therefore cause us to reject the reported detection of SF₆.

2.5 Nitrogen and Nitrogen Compounds

2.5.1 Molecular Nitrogen

Molecular nitrogen is the second most abundant constituent of the Venusian atmosphere. Its presence was first deduced from gas absorption experiments on the Venera 4,5,6 spacecraft which determined the sum of N₂ + inert gases by difference after the CO₂ was removed by chemical absorption. These results gave N₂ mixing ratios of $\leq 2\%$ (e.g., Vinogradov *et al* 1971). As noted by von Zahn *et al* (1983), the subsequent more sophisticated N₂ analyses by the Pioneer Venus and Venera 11/12 mass spectroscopy and gas chromatography experiments gave higher N₂ mixing ratios (see Table 1). However,

the values determined by the Pioneer Venus gas chromatograph, the Venera 11/12 mass spectrometer, and the Venera 11/12 gas chromatograph do not agree within the stated uncertainties. Furthermore, the Pioneer Venus gas chromatography results show an apparent decrease in N_2 with decreasing altitude ($4.60 \pm 0.14\%$ at 52 km, $3.54 \pm 0.04\%$ at 42 km, and $3.41 \pm 0.01\%$ at 22 km). These data were critically assessed by von Zahn *et al* (1983) who gave a recommended value of $3.5 \pm 0.8\%$ below 45 km altitude, which is adopted here.

2.5.2 Ammonia

Surkov *et al* (1974) reported that the Venera 8 spacecraft detected ammonia in the atmosphere of Venus at mixing ratios from 100 to 1,000 ppm. This detection was based on the color change observed when Venusian atmospheric gas reacted with bromophenol blue (tetrabromophenol-sulphaphthalein), a pH indicator which turns blue on exposure at basic pH values. The spacecraft measurements were done at 44 km (2 bars) and 32 km (8 bars).

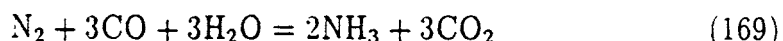
This reported detection of NH_3 is in conflict with significantly lower upper limits determined by Earth-based and Earth-orbital spectroscopic observations in the ultraviolet, infrared, and microwave regions. Benedict (1968, quoted in Goettel and Lewis 1974) gave an upper limit of 50 ppb from infrared spectroscopy, Owen and Sagan (1972) gave an upper limit of 0.1 ppm from ultraviolet spectroscopy, and Smirnova and Kuz'min (1974) gave an upper limit of 16 ppm from microwave spectroscopy. The first two values refer to the cloud top region while the microwave value is for the lower atmosphere below the clouds.

The reported NH_3 abundance is also in conflict with thermodynamic predictions. From a consideration of the equilibrium



and observational upper limits on CO and H_2O , which allowed him to thermodynamically calculate an upper limit on the H_2 partial pressure, Mueller (1964b) concluded "that no significant quantity of ammonia can occur if P_{N_2} has any reasonable value for a terrestrial planet of this size." However Mueller (1964b) did not actually present any calculated upper limits for NH_3 on Venus.

After the Venera 8 results were reported, a more quantitative argument against NH_3 was made by Goettel and Lewis (1974) who noted that the reported detection of NH_3 disagreed with the abundance predicted from the thermochemical reaction



which has the equilibrium constant

$$\log_{10} K_{169} = -17.39 + 11396(\pm 54)/T \quad (170)$$

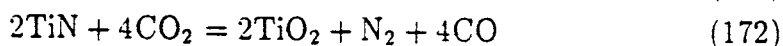
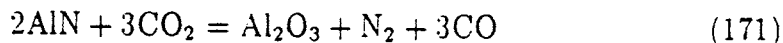
from 298 to 800 K. For example, at 740 K, where gas phase equilibrium is most likely to be attained, reaction (169) yields a NH_3 mixing ratio of

$\sim 10^{-28}$, orders of magnitude below the reported values. As Figure 1 of Goettel and Lewis (1974) illustrates, the equilibrium NH_3 mixing ratio increases rapidly with decreasing temperature. However, reaction (169) is probably kinetically inhibited at low temperatures and equilibrium cannot be attained. But in any case, Goettel and Lewis (1974) also emphasized that the maximum NH_3 mixing ratio is limited by the amounts of CO and H_2O in the Venusian atmosphere. The CO mixing ratios of 20–30 ppm observed below the clouds (Oyama *et al* 1980; Gel'man *et al* 1979) and the stoichiometry of reaction (169) limit the maximum NH_3 mixing ratio to 13–20 ppm. The reported mixing ratios of 100 to 1000 ppm are thus physically impossible. Florensky *et al* (1977) also present calculations (their Figure 1) which also illustrate that the reported NH_3 mixing ratios violate mass balance constraints.

Finally, it should be noted that Young (1977) has proposed a more plausible explanation for the Venera 8 results. He pointed out that bromophenol blue turns violet red in concentrated H_2SO_4 and speculated that the Venera 8 experiment had actually reacted with the concentrated sulfuric acid which makes up the cloud droplets. Young's observation in concert with the spectroscopic upper limits and the chemical arguments lead us to reject the Venera 8 result as an experimental artifact.

2.5.3 N-Bearing Minerals

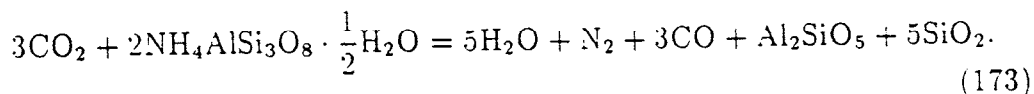
There is no observational evidence for any nitrogen-bearing minerals on the surface of Venus. Furthermore, theoretical arguments suggest that pure nitrogen-bearing phases are unlikely to be present on the Venusian surface. For example, nitride minerals, if present, would spontaneously be oxidized via reactions such as



with the overlying atmosphere. Likewise, pure nitride minerals are also thermodynamically unstable on the Earth. However, the small amounts (~ 10 –100 ppm) of nitrogen which are commonly found in igneous and metamorphic minerals on the Earth (reviewed by Wlotzka 1970) may be present as dissolved nitrides and/or oxynitrides. By analogy with the Earth, a similar situation is also expected on Venus. The dissolved nitrogen is probably unimportant from the perspective of atmosphere–surface chemistry but may nevertheless constitute a significant fraction of the nitrogen inventory on Venus.

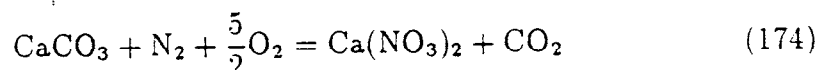
Other possible N-bearing minerals are ammonium silicates. One well known example is the ammonium silicate buddingtonite $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$, which has been synthesized under hydrothermal conditions (550–650°C, 2 kbars) by Barker (1964) and which occurs naturally as pseudomorphs after plagioclase in andesitic rocks which have been hydrothermally altered by NH_3 -rich hot-spring waters (Erd *et al* 1964). No experimentally determined thermodynamic data are available to quantitatively assess the stability of buddingtonite under Venusian surface conditions. However, the conditions

required for buddingtonite synthesis in the laboratory and its natural occurrences suggest that buddingtonite would be unstable on the Venusian surface because of the low water vapor partial pressures. One possible decomposition reaction is



Other NH_4^+ -bearing minerals are micas and clay minerals (Wlotzka 1970). However, we also expect that these minerals will decompose under the high temperatures and low water vapor partial pressures present at the surface of Venus.

Finally, by analogy with the Earth where nitrate ions are sometimes found in solid solution in calcite (Wlotzka 1970) one may ask whether nitrate might also be found dissolved in carbonates on Venus. We have examined this possibility by studying the reaction



which has the equilibrium constant

$$\log_{10} K_{174} = -20.37 + 6528(\pm 145)/T. \quad (175)$$

This was calculated using data from Parker *et al* (1971) for $\text{Ca}(\text{NO}_3)_2$. Rearranging the equilibrium constant expression for reaction (175) yields

$$(a_{\text{nitrate}}/a_{\text{calcite}}) \sim 10^{-67} \quad (176)$$

at 740 K. Thus nitrate solid solution in carbonate can safely be neglected under Venusian surface conditions.

The arguments above therefore lead us to conclude that no nitrogen-bearing minerals are stable anywhere on the Venusian surface. As mentioned before small amounts of nitrogen may be dissolved in silicate minerals, but if present these substitutions are unlikely to be important for atmosphere-surface chemical interactions.

3 Summary and Recommendations for Future Work

We have attempted to give a quantitative discussion as well as a critical review of the chemical interactions between the atmosphere and surface of Venus. The results of our calculations have been used to predict stable minerals and mineral assemblages on the surface of Venus, to determine which, if any, atmospheric gases are being buffered by mineral assemblages on the surface, and to critically review and assess the extensive literature dealing with atmosphere-surface chemistry on Venus. We want to summarize this discussion by presenting what we feel are the important issues facing us today

about atmosphere-surface chemistry on Venus and to recommend specific experimental, observational, and theoretical studies which can improve our knowledge of these issues.

The important issues in atmosphere-surface chemistry on Venus and our recommendations for addressing these questions include the following:

(1) The mineralogical composition of the surface of Venus is presently unknown. This information is crucial to understanding the chemical interactions between the atmosphere and surface of this planet and needs to be determined by spacecraft missions. We recommend development of a X-ray diffraction experiment suitable for spacecraft operations in order to address this issue. Many of the questions currently facing us about gas-solid reactions on Venus can be solved with a knowledge of the presence and abundance of the major rock-forming minerals.

(2) As noted by other authors such as Lewis, the CO_2 pressure on Venus is identical within the uncertainties in the thermodynamic data to the CO_2 equilibrium partial pressure developed by the calcite + wollastonite + quartz assemblage at the mean Venus surface temperature of 740 K. However, the rate of this reaction under Venusian surface conditions is not known and needs to be measured experimentally to determine if this important reaction is indeed capable of buffering CO_2 on Venus. These measurements need to be made so that the dependence of the reaction rate on important variables (e.g., temperature, mineral surface area, water vapor partial pressure, etc.) is determined and can be extrapolated and/or interpolated to Venusian surface conditions. The rate and mechanism of both the decarbonation and carbonation reactions need to be studied.

(3) Several authors (e.g., Florensky *et al* 1977; Nozette and Lewis 1982) have proposed that a combination of chemical and physical weathering on mountaintops can provide to the lowlands regions on Venus the calcium-rich mineral assemblages theoretically predicted to be necessary for buffering reactions such as the calcite + wollastonite + quartz equilibrium. However, essentially no information is available on the efficiency of physical weathering for removing the chemically reacted outer layers from mineral grains under Venusian surface conditions. We recommend experimental studies using facilities such as the Venus Wind Tunnel at the NASA Ames Research Center to measure quantitatively these efficiencies.

(4) Chemical equilibrium calculations using the published thermodynamic data on scapolite minerals predict that meionite (CO_3^{2-} -bearing scapolite) and sulfate meionite are unstable on the surface of Venus but that marialite (Cl -bearing scapolite) is stable on the surface. However, the Semenov *et al* (1981) thermodynamic data on marialite cannot be accepted uncritically and we recommend calorimetric measurements of the low temperature heat capacity, high temperature heat content, and the heat of formation of well characterized natural mineral samples having a known ordering state. These measurements could be supplemented by retrieval of the thermodynamic properties of marialite from phase equilibrium experiments.

(5) The f_{O_2} of the Venusian lower atmosphere and surface is controlled by the CO/CO_2 ratio, and is inside the magnetite stability field. However,

as argued by Pieters *et al* (1986), spectral reflectivity measurements made by several Venera spacecraft imply that hematite is present on the surface of Venus. This apparent inconsistency with the thermodynamic predictions may reflect kinetic inhibition of the hematite→magnetite conversion or the existence of a stable Fe^{3+} -bearing mineral on the surface of Venus. These questions can be answered by experimental measurements under the appropriate conditions of the rate of the hematite→magnetite conversion and of the kinetics and mechanism of olivine oxidation in CO/CO_2 gas mixtures.

(6) No pure hydrated silicates for which thermodynamic data are available are predicted to be thermodynamically stable on the Venusian surface. The possible exceptions are tremolite and phlogopite which may be stable at altitudes higher than those observed by the Pioneer Venus radar altimetry experiment. The question of tremolite and phlogopite stability can be clarified by improved measurements of their thermodynamic properties in order to decrease the large uncertainties in the existing thermodynamic data. The question of stabilities of other hydrated silicates can be clarified by experimental studies of the thermodynamic properties of some amphibole and hornblende minerals that are believed to be more stable than the hydrated silicates for which data are available. The amphiboles and hornblendes which we recommend studying are edenite, some members of the richterite family, and some alkali amphiboles (e.g., see Gilbert *et al* 1982).

(7) The chemical interactions of sulfur gases and sulfur-bearing minerals on the Venusian surface is still only poorly understood. However, it is nevertheless clear that chemical equilibrium models are inapplicable to sulfur gas-solid chemistry on Venus. Observational data indicate that atmospheric abundance of SO_2 is significantly higher than the predicted chemical equilibrium value. Laboratory reaction rate measurements for one reaction, anhydrite formation from SO_2 + calcite, show that it is too slow to reduce the SO_2 abundance down to the chemical equilibrium value, thus providing a possible explanation for the observations. However, no quantitative kinetic data are available for the reactions of SO_2 with calcium-bearing igneous minerals on the Venusian surface. We recommend experimental measurements of the kinetics and mechanisms of the reactions of SO_2 with diopside, anorthite, and wollastonite under appropriate conditions to enable extrapolation and/or interpolation of the laboratory rate data to Venusian surface conditions.

(8) Radar observations from Earth-based sites, the Pioneer Venus spacecraft, and the Magellan spacecraft show the presence of radar "bright" regions in the highland areas of Venus. These areas have been suggested to be pyrite (e.g., Pettengill *et al* 1982) and subsequent work suggested a volumetric abundance of ~14% (Pettengill *et al* 1988). However, preliminary data on the rate of pyrite oxidation under Venusian surface conditions (Fegley and Treiman 1990) indicate that this mineral is very rapidly weathered at the rate of 3–20 cm per year on the Venusian surface, and is thus unlikely to be present for extended time periods. In order to resolve this apparent discrepancy we recommend several types of studies. One of these is further laboratory studies of the kinetics of iron sulfide (e.g., pyrite, pyrrhotite) weathering under Venusian surface conditions. Another study is a laboratory

investigation of the radar properties of possible analogs to the radar "bright" regions on Venus. On the basis of the estimated volumetric abundance of pyrite in radar "bright" regions on Venus, analog materials are probably natural samples rich in iron-bearing oxides and sulfides such as lunar basalts rich in ilmenite, magmatic sulfides from terrestrial deposits, and magnetite-rich terrestrial basalts.

(9) Finally, the abundances of HCl and HF in the Venusian atmosphere are probably buffered by mineral assemblages on the Venusian surface, although the assemblages suggested previously in the literature (Lewis 1970a) are incorrect because they involve thermodynamically unstable or metastable assemblages. We recommend experimental studies of the thermodynamics and kinetics of the new buffers proposed in this paper. All these buffers involve stable mineral assemblages observed in different rock types on the Earth, and thus any experimental studies will yield information relevant to terrestrial petrology as well as to Venus.

4 Acknowledgments

We acknowledge support from the Lunar and Planetary Institute, Houston, TX and the Max Planck Institut für Chemie, Mainz, Germany (B.F.) and from the National Research Council and the NASA Johnson Space Center (A.T.). Our experimental work on Venus surface-atmosphere chemistry is currently supported by a grant from the NASA Planetary Atmospheres Program (B. Fegley, P.I.). We thank B. Bézard, C. DeBergh, E. Essene, T. Spohn, and D. Sverjensky for preprints. We also acknowledge discussions with B. Bézard, C. DeBergh, K. Lodders, E. Shock and H. Wänke. Finally, we thank M.Ya. Marov for the invitation to submit this paper.

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