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The sulfur vapor pressure over pyrite on the surface of Venus

Yong Hong and Bruce Fegley, Jr.

Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Campus Box 1169, Washington University, One Brookings Drive, St. Louis, MO 63130-4899, U.S.A.

**Abstract.** The total pressure and molecular speciation of sulfur vapor (dominantly S_2) over pyrite at Venus surface temperatures (≈ 390–$470°C$) are important for modeling atmospheric chemistry and geochemistry of sulfur gases and minerals on Venus. The sulfur vapor pressure over pyrite in CO_2 and CO_2 gas mixtures, which are relevant to Venus, has not been previously measured. Instead, previous measurements were generally done in closed systems, such as sealed, evacuated silica tubes. We measured the sulfur vapor pressure over pyrite in an open system where carrier gas is flowing through a gas mixing furnace, from 441 to 591°C in He, N_2, CO_2, and CO_2–SO_2–CO mixtures using a standard technique, the transpiration method (Merton, U. and Bell, W. E. (1967) The transpiration method. In *The Characterization of High Temperature Vapors*, ed. J. W. Margrave, pp. 91–114. Wiley, New York). The data show that the sulfur vapor pressure over pyrite is the same in inert gas and in CO_2-bearing gases. Our data also agree with literature vapor pressure data. Thermodynamic calculations show that the laboratory vapor pressure data are also valid at Venus surface pressures (≈ 50–100 bar). Finally, we present recommended values for the sulfur vapor pressure and calculate the molecular speciation of sulfur vapor over pyrite at Venus surface temperatures. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

Pyrite (FeS_2) chemical weathering was predicted by Von Zahn *et al.* (1983) and Prinn (1985) to be an important source of reduced sulfur gases on Venus. They suggested that pyrite reacted with CO_2 and CO in Venus' atmosphere to generate OCS by the reaction:

$$FeS_2 + CO_2 + CO \rightarrow FeO + 2OCS \qquad (1)$$

However, at the time no experimental data on reaction (1) were available to test their predictions. Subsequently, Fegley *et al.* (1995) studied pyrite decomposition in CO_2 and CO_2 gas mixtures at Venus surface temperatures (≈ 660–740 K or ≈ 390–$470°C$) and found that pyrite thermally decomposed via the reaction

$$7FeS_2(\text{pyrite}) = Fe_7S_8(\text{pyrrhotite}) + 3S_2(\text{gas}) \qquad (2)$$
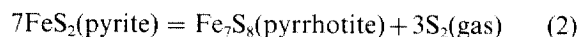
instead of being oxidized via reaction (1). At the global mean surface temperature of 740 K on Venus the Fe–S phase diagram predicts that the Fe/S ratio of pyrrhotite should be 0.875 (Stølen and Grønvold, 1987), corresponding to Fe_7S_8. Fegley *et al.* (1995) showed by X-ray diffraction and Mössbauer spectroscopy that at 740 K pyrite decomposes to Fe_7S_8, in agreement with the expected Fe/S ratio (Stølen and Grønvold, 1987). Fegley *et al.* (1995) also proposed that reaction (2) is a source of sulfur vapor in Venus' lower atmosphere. Their suggestion is illustrated in Fig. 1, which shows the gas–aerosol, gas phase, and gas–rock reactions in the Venus sulfur cycle.

Here we present sulfur vapor pressure measurements for reaction (2), expanding upon the kinetic data reported by Fegley *et al.* (1995) and the preliminary sulfur vapor pressure data presented by Hong *et al.* (1996) at the December 1996 AGU meeting. We find that pyrite thermally decomposes to pyrrhotite and sulfur vapor via reaction (2) in inert gas, CO_2 and CO_2–CO–SO_2 gas mixtures.

The sulfur vapor pressure over pyrite has been measured with a variety of other methods including dew point, manometric, electrum tarnish, and electromotive force measurements instead of weight loss measurements (see Table 1). Previous measurements were generally done in closed systems, such as sealed, evacuated silica tubes. In contrast, our data are from experiments in an open system where a carrier gas is flowing through a gas mixing furnace. Our results are important because the sulfur vapor pressure over pyrite in CO_2 and CO_2 gas mixtures, which are relevant to Venus, has not been measured.

Correspondence to: B. Fegley Jr. Tel.: (+1) (314) 935 4852; fax: (314) 935 4853; e-mail: bfegley@levee.wustl.edu.
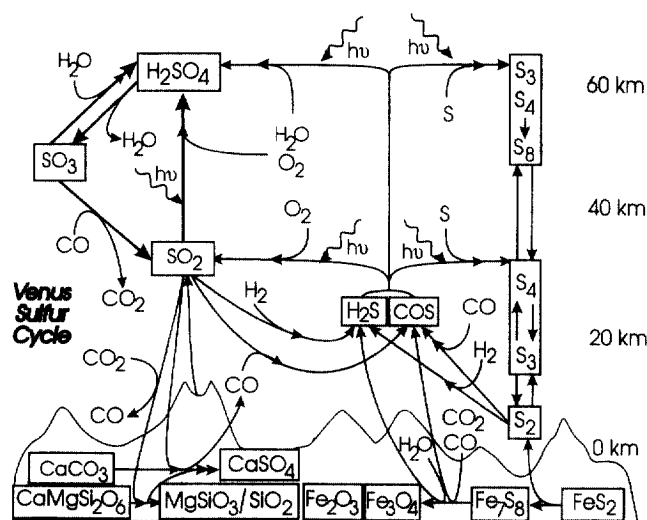
Fig. 1. The gas–aerosol, gas phase, and gas–rock reactions in the Venus sulfur cycle. This expanded and revised picture of the sulfur cycle, originally proposed by Von Zahn *et al.* (1983) and Prinn (1985), incorporates experimental data showing that pyrite thermally decomposes to pyrrhotite (Fe_7S_8) and sulfur vapor on Venus' surface (Fegley *et al.*, 1995). The gas–rock reactions that are sinks for SO_2 are discussed by Fegley *et al.* (1997)

Table 1. Literature data for the vapor pressure of pyrite

Authors	Method[a]	Temperature range (°C)
This Work	transpiration	441–591
Allen and Lombard, 1917	dew point	575–680
Barker and Parks, 1986	a literature review	300–743
Bog and Rosenqvist, 1959	manometry	500–552
Dickson *et al.*, 1962	dew point	647–681
Giletti *et al.*, 1968	radioactive S isotopes	420–600
Juza and Biltz, 1932[b]	manometry	629–669
D'Or, 1931	manometry	548–676
Raeder, 1929	manometry	590–686
Rau, 1976	manometry	547–1101
Rudder, 1936	manometry	600–689
Schneeberg, 1973	sulfur vapor sensor	324–438
Toulmin and Barton, 1964	electrum tarnish	325–743

[a] Different manometric methods were used by different authors and we refer the reader to the original papers for more detailed descriptions of experimental design.
[b] Four data points in fairly good agreement with other manometry measurements. The data are not shown in Fig. 4 because of space limitations.

Our results support the proposal of Fegley *et al.* (1995) that pyrite composition on Venus' surface occurs by reaction (2). Furthermore our data can be applied to modeling the atmospheric chemistry and geochemistry of sulfur compounds on Venus, to the interpretation of the sulfur vapor observations made by spectrophotometers on the Venera 11–14 spacecraft (Von Zahn *et al.*, 1983; Krasnopolsky, 1987), and to the design of geochemical experiments on future spacecraft missions to Venus. These applications will be described elsewhere.

Measurements of the sulfur vapor pressure over pyrite

General procedure

We measured the sulfur vapor pressure over pyrite using the transpiration method, which is a standard technique in physical chemistry (Merton and Bell, 1967). A schematic diagram of the experimental apparatus is shown in Fig. 2. The experiments were done by passing a carrier gas, at controlled flow rate for known times, over pyrite samples that were isothermally heated at different temperatures in a furnace. We used He, N_2, CO_2, and CO_2 gas mixtures as carrier gases, and regulated the carrier gas pressure to be ≈ 1 bar. We calculated the temperature-dependent sulfur vapor pressures (P_{S2}) from the equation:

$$P_{S_2} = n_{S_2}/(n_{S_2} + n_c)P = X_{S_2}P \qquad (3)$$

where P_{S_2} is the S_2 vapor pressure over pyrite, P is the total pressure (1 bar), n_{S_2} is the number of moles of S_2 vapor, n_c is the number of moles of carrier gas, and X_{S_2} is the mole fraction of S_2 vapor in the gas. The moles of S_2 vapor evolved are calculated from the observed weight loss of the pyrite after heating. The moles of carrier gas used are calculated from the duration of the experiment and the STP (standard temperature, 273 K, and pressure, 1 bar) flow rate.

Sulfur vapor is composed of allotropic species $(S, S_2, S_3, S_4, S_5, S_6, S_7, S_8)$, but experimental studies of sulfur vapor show that S_2 is the dominant gas at the pressures and temperatures used in our experiments. These experimental studies are summarized on pp. 265–286 in vol. 1 of Gurvich *et al.* (1989–1994). Thus, the n_{S_2} term is easily calculated from the weight loss because the sulfur vapor evolved from the heated pyrite samples is dominantly S_2 gas. We return to this point later when we use thermodynamic data for S-S_8 gases to calculate the molecular speciation of sulfur vapor above pyrite at Venus surface temperatures.

Experimental details

Pyrite from Zacatecas, Mexico and Huanzala, Peru was used for our measurements. The pyrite samples were char-
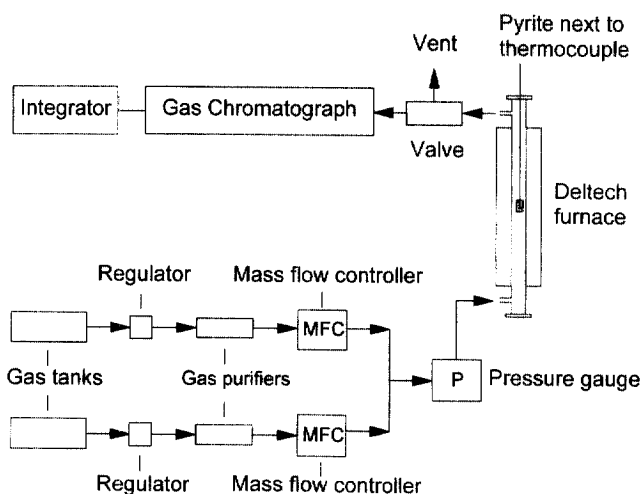
Fig. 2. A schematic diagram of the experimental apparatus used in the transpiration experiments. See the text for a description

acterized by X-ray diffraction (XRD), electron micro-probe analysis, gravimetric analyses by quantitative combustion to hematite, reflected light microscopy, and density measurements on carefully weighed and measured pieces. The XRD patterns are identical to that of pyrite (JCPDS pattern 42-1340). Electron microprobe analyses gave 46.16±0.80% Fe and 53.32±0.68% S (mean of 19 analyses with 2σ errors) in good agreement with the values of 46.55% Fe and 53.45% S for stoichiometric pyrite. Gravimetric analyses gave 2.001±0.001(2σ) and 2.000± 0.001(2σ) for the S/Fe atomic ratios of the Mexican and Peruvian pyrite, respectively. The operating conditions for the electron microprobe analyses and XRD patterns are given by Fegley et al. (1995). Reflected light microscopy of several samples did not show any other phases. The measured densities are 4.92 g cm^{-3} and 4.89 g cm^{-3}, respectively, for the Peruvian and Mexican pyrite, in agreement with the densities of 4.89–5.03 g cm^{-3} listed by Deer et al. (1963). The pyrite samples are pure, stoichiometric FeS$_2$.

Pyrite samples initially weighing ≈ 200–800 mg were hung by fine platinum wires in the isothermal hot zones of 1 atm gas mixing vertical tube furnaces (Deltech, Denver, CO). Calibrated Pt–Rh thermocouples measured the temperature right next to the samples. The samples were lowered into the hot zones of the furnaces after all air had been flushed from the system by the carrier gas flow. The absence of air was verified by gas chromatography. The samples typically reached the reaction temperature in 5 min or less, and then were heated at atmospheric pressure in the desired carrier gas. At the end of an experiment, the sample was raised to the cool top of the furnace, where the sample cooled within 5 min. The pyrite was then reweighed. X-ray diffraction and electron microprobe analyses verified that only pyrite and pyrrhotite were present in the reacted samples.

Helium (ultra high purity (UHP), 99.999%), N$_2$ (UHP, 99.999%), Coleman instrument grade CO$_2$ (99.99%), SO$_2$ (0.96%)–CO$_2$ (99.04%), or CO (54 ppmv)–SO$_2$ (0.48%)–CO$_2$ (99.52%) were used as carrier gases. The lower atmosphere of Venus contains 96.5% CO$_2$, 25–150 parts per million by volume (ppmv) SO$_2$ and 17–20 ppmv CO (Fegley et al., 1997). We used inert gases (He, N$_2$), CO$_2$ and CO$_2$ mixtures to determine if reaction (1) is important and if CO$_2$, SO$_2$ and CO affect the sulfur vapor pressure over pyrite on Venus.

The carrier gases were passed through hot copper turnings and magnesium perchlorate (Mg(ClO$_4$)$_2$) to remove any O$_2$ and H$_2$O impurities in them. No O$_2$ or H$_2$O were found by gas chromatography at our detection limit (≈ 1 ppmv) in the purified gases. The gas flow rate was controlled at 150 cm^3 min^{-1} (STP) by calibrated electronic mass flow controllers (Tylan Corporation) and calibrated rotameters. Preliminary work by Hong et al. (1996) showed that this flow rate is appropriate for the transpiration experiments and is neither too slow nor too fast (see Merton and Bell, 1967).

Gas chromatography (GC) was done using a Hewlett Packard 5890 Series II gas chromatograph with a thermal conductivity detector and either a Porapak Q or CTR I column. The GC carrier gas was UHP grade He, further purified using an Alltech Associates gas purifier, at a flow rate of 100 cm^3 min^{-1}. Gas lines connected the gas mixing boards and furnaces to an automated gas sampling valve on the gas chromatograph.

Experimental results

This work and comparison with literature data

The basic experimental data (temperature, time, weight loss) and the calculated S$_2$ vapor pressures over pyrite are given in Table 2 and are plotted in Fig. 3. There is good agreement between the pyrite vapor pressures measured in the inert gases (He, N$_2$), in CO$_2$, and the two CO$_2$ gas mixtures. Most of the data points fall on or very close to the linear regression fit to all data. We conclude that the pyrite vapor pressure is the same in inert gases, in CO$_2$, and CO$_2$ gas mixtures.

Pyrite vapor pressure measurements from the literature are summarized in Table 1. These data and our data are plotted in Fig. 4. There is good agreement between our data and the literature data even though none of the prior studies were transpiration experiments.

In general our vapor pressures almost exactly reproduce the data of other investigators (Toulmin and Barton, 1964; Schneeberg, 1973; Giletti et al., 1968; Bog and Rosenqvist, 1959; Rudder, 1936) at the same temperatures as we studied. Below about 500°C, our vapor pressure data are slightly higher than those of Toulmin and Barton (1964). However, Fig. 4 shows that the data of Toulmin and Barton (1964) may be systematically low below ≈ 500°C, as was also concluded by Barker and Parks (1986). Conversely, our lower temperature data agree better with Rau (1976) than do our higher temperature data. The lowest temperature points measured by Allen and Lombard (1917) and D'Or (1931) disagree with most of the data plotted on Fig. 3. We conclude that the low temperature data of Allen and Lombard (1917) and D'Or (1931) are respectively too low and too high.

The data in Figs 3 and 4 show that pyrite has the same vapor pressure in CO$_2$, CO$_2$ gas mixtures, inert gas, and in a closed system (such as a sealed, evacuated silica tube where sulfur vapor is the only gas present). GC analyses of the carrier gas flows leaving our furnaces support this conclusion. The GC analyses do not show other gases except for trace amounts of OCS formed in the CO-bearing gas mixtures. However, the calculated S$_2$/OCS molar ratios are > 100, so the formation of OCS does not affect the pyrite vapor pressure data.

Effect of total pressure on the sulfur vapor pressure over pyrite

On Venus, the atmospheric pressure and temperature vary from ≈ 96 bar and 740 K at the modal radius of 6051.4 km to ≈ 47 bar and 660 K at the top of Maxwell Montes. Thus, the sulfur vapor pressure over pyrite on Venus could be slightly higher than that measured in the laboratory, because the vapor pressure of a condensed phase is increased slightly by the presence of a second gas (pp. 204–207, Denbigh, 1992).

However, calculating the effect of total pressure on the

Table 2. Pyrite vapor pressure measurements

Run no.	Time (h)	Temperature (°C)	Weight loss (mg)	$P(S_2)$ (bar)	$\log_{10} P(S_2)$
Helium					
H138	66.0	464	5.267	6.20(−6)	−5.21
H137	66.0	490	24.988	2.92(−5)	−4.53
H142	4.2	522	5.881	1.08(−4)	−3.96
H143	4.2	551	41.843	7.74(−4)	−3.11
Nitrogen					
H165	90.2	475	22.915	9.86(−6)	−5.01
H166	24.0	502	38.049	6.15(−5)	−4.21
H167	41.0	502	55.205	5.22(−5)	−4.28
H169	4.25	536	31.312	2.86(−4)	−3.54
Carbon dioxide					
H27	92.0	441	6.388	2.70(−6)	−5.57
H28	64.0	465	24.090	1.46(−5)	−4.84
H25	20.0	509	129.961	2.52(−4)	−3.60
H26	5.1	529	66.217	5.04(−4)	−3.30
H36	109.0	460	18.732	6.67(−6)	−5.18
H75	161.5	460	29.933	7.20(−6)	−5.14
H58	44.0	479	34.923	3.08(−5)	−4.51
H53	14.0	480	8.332	2.31(−5)	−4.64
H50	22.8	480	19.627	3.34(−5)	−4.48
H68	64.0	481	58.062	3.52(−5)	−4.45
H63	16.3	505	49.924	1.19(−4)	−3.92
H60	3.0	532	39.962	5.17(−4)	−3.29
H87	17 min	579	35.774	4.90(−3)	−2.31
H86	22 min	591	81.567	8.64(−3)	−2.06
CO_2–SO_2 mixture					
H96	54.0	436	3.999	2.87(−6)	−5.54
H97	22.0	467	3.000	5.29(−6)	−5.28
H80	16.5	500	36.968	8.69(−5)	−4.06
H81	4.0	531	45.096	4.37(−4)	−3.36
CO_2–CO–SO_2 mixture					
H72	24.0	469	9.618	1.56(−5)	−4.81
H71	14.0	500	26.046	7.22(−5)	−4.14
H70	4.0	530	34.875	3.38(−4)	−3.47
H74	1.0	570	69.576	2.70(−3)	−2.57
H82	22 min	589	79.022	8.36(−3)	−2.08

[a] The numbers in parenthesis are exponents. Thus $4.7(−9)$ is 4.7×10^{-9} bar.

sulfur vapor pressure over pyrite is complex because pyrite evaporates incongruently and there are several components in the solid and gas (e.g. FeS_2, Fe_7S_8, S, S_2, S_3, S_4, S_5, S_6, S_7, S_8). As a first approximation, we consider the effect of pressure on the S_2 vapor pressure over liquid sulfur using the equation (Denbigh, 1992)

$$\left(\frac{\partial \log P_{S_2}}{\partial P_{tot}}\right)_T = \frac{v_m}{2.303RT} \qquad (4)$$

The molar volume of liquid sulfur is $v_m = 38.25 \text{ cm}^3 \text{mol}^{-1}$ or $53 \text{ cm}^3 \text{mol}^{-1}$ at 325 or 700°C, respectively, from Toulmin and Barton (1964). We calculate that the change in the pyrite vapor pressure (P_{S_2}) for a 100 bar change in the total pressure (P_{tot}) is $\Delta \log_{10} P_{S_2} \approx 0.033$ log units at 325°C (598 K) and 0.029 log units at 700°C (973 K). These changes in the sulfur vapor pressure over pyrite are insignificant.

Taking into account the effect of pressure on reaction

(2), Toulmin and Barton (1964) calculated the effect of total pressure on the sulfur vapor pressure over pyrite to be $\Delta \log_{10} P_{S_2} \approx 0.05$ at 325°C (598 K) to ≈ 0.03 at 700°C (973 K) for a 100 bar pressure increase. Thus, the 47–100 bar pressure at Venus' surface has a negligible effect on the sulfur vapor pressure over pyrite, and the laboratory vapor pressure data are relevant to Venus.

Molecular speciation of sulfur vapor

We calculated the molecular speciation of sulfur vapor as a function of temperature at the surface of Venus. This was done by solving the mass balance equation:

$$P_{vap} = P_S + P_{S_2} + P_{S_3} + P_{S_4} + P_{S_5} + P_{S_6} + P_{S_7} + P_{S_8} \qquad (5)$$

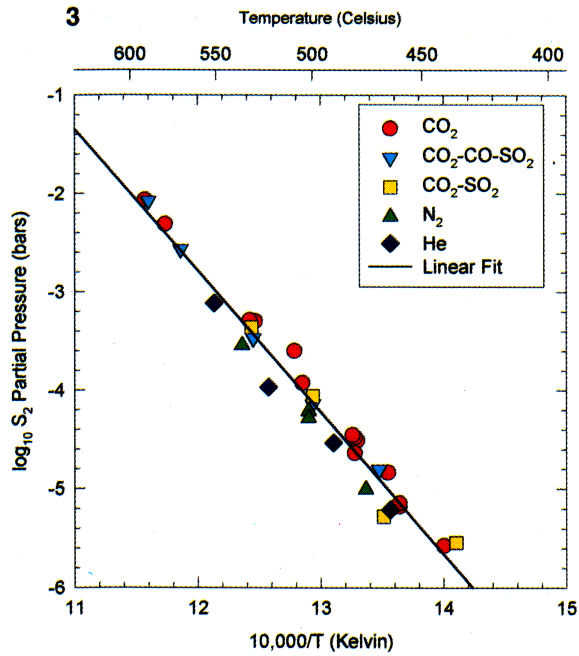using the equilibrium constants given by Gurvich et al. (1989–1994) and the vapor pressure over pyrite (P_{vap})

Fig. 3. Results of the transpiration experiments in He, N_2, CO_2, and two CO_2 gas mixtures: 0.96% SO_2 in CO_2 and 54 ppmv CO, 0.48% SO_2 in CO_2. The sulfur vapor pressure over pyrite is the same in inert gas (He, N_2), CO_2, and CO_2-bearing gas. As discussed in the text, S_2 is the major gas in sulfur vapor for our experimental conditions
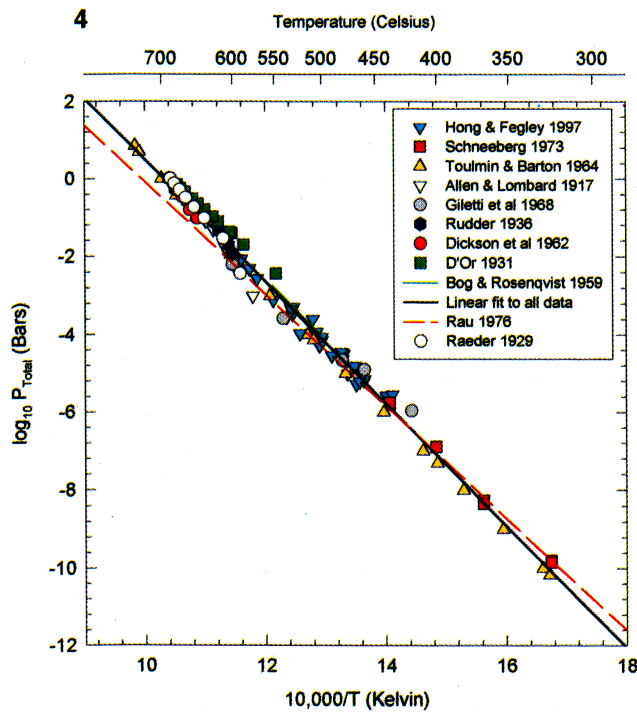

Fig. 4. A comparison of our data and literature data. Bog and Rosenqvist (1959) give an equation, but no data points. The results of Rau (1976) are also shown as a linear fit. See Barker and Parks (1986) for a description of Rau's data

Table 3. The sulfur vapor pressure (bar) over pyrite at Venus surface temperatures [a]

Temperature (K)	S	S_2	S_3	S_4	S_5	S_6	S_7	S_8	$\%S_2$
640	2.2(19)	4.7(−9)	1.0(−12)	6.4(−16)	2.4(−17)	2.5(−19)	1.5(−22)	5.0(−25)	99.98
660	1.8(−18)	2.6(−8)	1.0(−11)	1.0(−14)	6.1(−16)	8.7(−18)	9.3(−21)	4.8(−23)	99.96
680	1.3(−17)	1.3(−7)	8.8(−11)	1.3(−13)	1.3(−14)	2.5(−16)	4.5(−19)	3.6(−21)	99.93
700	8.0(−17)	6.0(−7)	6.7(−10)	1.5(−12)	2.3(−13)	5.8(−15)	1.7(−17)	2.0(−19)	99.89
720	4.6(−16)	2.5(−6)	4.6(−9)	1.5(−11)	3.4(−12)	1.2(−13)	5.5(−16)	9.4(−18)	99.82
740	2.4(−15)	9.7(−6)	2.8(−8)	1.3(−10)	4.4(−11)	1.9(−12)	1.4(−14)	3.5(−16)	99.71
760	1.1(−14)	3.5(−5)	1.6(−7)	1.0(−9)	5.0(−10)	2.8(−11)	3.2(−13)	1.1(−14)	99.55

[a] The numbers in parenthesis are exponents. Thus $47(−9)$ is 47×10^{-9} bar.

calculated from the linear least squares fit to all data in Fig. 4:

$$\log_{10} P_{vap}(\text{pyrite}) = 16.20(\pm 0.21) - 15\,700(\pm 150)/T \quad (6)$$

Eqn (6), with 1σ uncertainties, is valid from 325 to 743°C and is our recommended equation for the sulfur vapor pressure over pyrite. Eqn (5) was solved iteratively using the mass balance, mass action algorithm described by Fegley and Lodders (1994).

The results of these calculations are given from 640 to 760 K in Table 3. This temperature range spans the range of temperatures on the surface of Venus. It is apparent that S_2 makes up $>99.5\%$ of the sulfur vapor pressure over pyrite at these temperatures. The second most abundant gas is S_3, but its abundance is only 0.5% or less of the total sulfur vapor pressure at these temperatures. The other allotropes are even less abundant than S_3 gas.

Summary

The sulfur vapor pressure over pyrite at Venus surface temperatures was measured using the transpiration method, a standard technique in physical chemistry. The results are the same in inert gas (He, N_2), CO_2, and CO_2–CO–SO_2 gas mixtures simulating the lower atmosphere of Venus. The data are also in good agreement with literature data. Thermodynamic calculations show that the ≈ 100 bar pressure on Venus does not change significantly the sulfur vapor pressure over pyrite. A recommended vapor pressure equation for pyrite is presented and used to calculate the molecular speciation of sulfur vapor over pyrite for Venus surface temperatures. The applications of the experimental data to modeling sulfur atmospheric chemistry and geochemistry on Venus and to the interpretation of atmospheric composition measurements from US and Russian space probes will be described elsewhere.

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