THERMODYNAMICS OF SILICON-HYDROXIDE FORMATION IN H₂O CONTAINING ATMOSPHERES

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ABSTRACT

The formation of volatile silicon-hydroxide species from SiO₂ in water containing atmospheres has been identified as a potentially important mode of degradation of Si-based ceramics. Availability of thermodynamic data for these species is a major problem. This study is part of an ongoing effort to obtain reliable, experimentally determined thermodynamic data for these species. The transpiration method was used to measure the pressure of Si-containing vapor in equilibrium with SiO₂ (cristobalite) and Ar + H₂O(g) with various mole fractions of water vapor, X₇H₂O, at temperatures ranging from 1000 to 1780 K. Enthalpies and entropies for the reaction, SiO₂(s) + 2H₂O(g) = Si(OH)₄(g), were obtained, at X₇H₂O = 0.15 and 0.37, from the variation of lnK with 1/T according to the “second law method”. The following data were obtained: \( \Delta H^\circ = 52.9 \pm 3.7 \text{ kJ/mole} \) and \( \Delta S^\circ = -68.6 \pm 2.5 \text{ J/moleK} \) at an average temperature of 1550 K, and \( \Delta H^\circ = 52.5 \pm 2.0 \text{ kJ/mole} \) and \( \Delta S^\circ = -69.7 \pm 1.5 \text{ J/moleK} \) at an average temperature of 1384 K, for X₇H₂O = 0.15 and 0.37, respectively. These data agree with results from the literature obtained at an average temperature of 1600 K, and strongly suggest Si(OH)₄(g) is the dominant vapor species. Contradictory results were obtained with the determination of the dependence of Si-containing vapor pressure on the partial pressure of water vapor at 1187 and 1722 K. These results suggested the Si-containing vapor could be a mixture of Si(OH)₄ + SiO(OH)₂. Further pressure dependent studies are in progress to resolve these issues.

INTRODUCTION

Silicon based ceramics (SiC and Si₃N₄) and molybdenum-disilicide intermetallics are proposed for structural applications above 1400 K in combustion environments. The long-term resistance of these materials to environmental degradation depends on the formation and retention of a thin protective SiO₂ layer. It has long been known that SiO₂ forms stable volatile silicon-hydroxide and -oxyhydroxide species in high-temperature high-pressure steam atmospheres (1). More recently this behavior was identified as a potentially important mode of degradation of the protective scale in combustion environments (2-4), which typically contain about 10% H₂O over a temperature range of 1073 to 1773 K at total pressures of 0.5 to 10 atm. A major problem encountered in understanding and modeling this degradation process is the limited amount of experimental thermodynamic data for silicon-hydroxide and -oxyhydroxide species. Krikorian (1) reviewed the research in the SiO₂-steam system prior to 1970 and proposed Si(OH)₄(g), Si₂O(OH)₆(g) and SiO(OH)₂(g) as the...
most likely volatile Si-containing species for the following range of conditions: 600 to 900 K at 1-to-100 atm, 600 to 900K at 2000-to-9000 atm, and 1760 K at 0.5-to-1 atm, respectively. Thermodynamic data were estimated for these species by combining the fugacity data of Si-containing species and \( \text{H}_2\text{O}(g) \) over a range of temperatures determined by both flowing and static experiments together with assumptions about bond energies and entropies of reaction. A more recent experimental study by Hashimoto (5) used the transpiration method to identify \( \text{Si(OH)}_4(g) \) as the dominant vapor species at ~1770 K in a carrier gas consisting of 0.5 atm \( \text{H}_2\text{O} / \text{balance } \text{O}_2 \). The enthalpy and entropy of the reaction to form \( \text{Si(OH)}_4(g) \) from \( \text{SiO}_2 \) and \( \text{H}_2\text{O}(g) \) were determined, at about 1600 K, to be 56.7±1.7 kJ/mol and -66.2±1.0 J/molK respectively. In the most recent experimental study, Hildenbrand and Lau (6) used Knudsen cell mass spectrometry (KCMS) with a “gas leak cell” to study the reaction between \( \text{SiO}_2(l) \) and \( \text{H}_2\text{O}(g) \) near 2000 K at \( P(\text{H}_2\text{O}) \) less then \( 5.0 \times 10^{-4} \) atm. \( \text{SiO(OH)}(g) \) and \( \text{SiO(OH)}_2(g) \) were the only stable volatile oxyhydroxide species under these conditions. Unfortunately this method cannot be used at higher vapor pressures. In a recent theoretical study, Allendorf et al. (7) calculated a set of self-consistent thermodynamic functions for 47 possible molecules in the Si-O-H system.

The formation of the four important vapor species from \( \text{SiO}_2 \) and \( \text{H}_2\text{O}(g) \) are summarized in equations [1]-[4]. There are still some questions regarding their stability as they have not all been directly identified with either spectroscopic or mass spectrometric evidence over an extended range of conditions. Recent mass spectrometric evidence, obtained using a high pressure sampling mass spectrometer at this laboratory (3), supports the stability of \( \text{Si(OH)}_4(g) \) and gave some evidence for \( \text{SiO(OH)}_2(g) \). There is no direct evidence for \( \text{Si}_2\text{O(OH)}_6(g) \).

\[
\begin{align*}
\text{SiO}_2(s) + 1/2\text{H}_2\text{O}(g) &= \text{SiO(OH)}(g) + 1/4\text{O}_2(g) \quad [1] \\
\text{SiO}_2(s) + \text{H}_2\text{O}(g) &= \text{SiO(OH)}_2(g) \quad [2] \\
\text{SiO}_2(s) + 2\text{H}_2\text{O}(g) &= \text{SiO(OH)}_4(g) \quad [3] \\
2\text{SiO}_2(s) + 3\text{H}_2\text{O}(g) &= \text{Si}_2\text{O(OH)}_6(g) \quad [4]
\end{align*}
\]

All available experimental and calculated data for the Si-O-H system has been compiled by Opila et al. (2) in a ChemSage (8) database. This has been used to predict the composition of the vapor phase as a function of temperature and the mole fraction of water vapor. An example is shown in figure 1 for \( X_{\text{H}_2\text{O}} = 0.37 \). In this figure two sets of data (K –data based on the Krikorian’s estimates and A –data based on Allendorf’s calculations) have been plotted. Both sets of data have used Hashimoto’s results for \( \text{Si(OH)}_4 \). Clearly there is a large discrepancy between the two regarding the importance of \( \text{SiO(OH)}_2 \). If the data based on Krikorian estimates based data are considered, the dominant vapor species changes from \( \text{Si(OH)}_4(g) \) at low temperatures to \( \text{SiO(OH)}_2(g) \) at high temperatures over the range 1000-to-1800 K. This presents a major difficulty for vapor pressure techniques that cannot separate complex vapor mixtures. In this study vapor pressure measurements of volatile Si-containing species were made using the transpiration method with an apparatus design similar to that of Hashimoto (5). Recognizing the potential difficulty in studying complex vapor mixtures, two series of measurements were proposed: 1) at low temperatures and high \( P(\text{H}_2\text{O}) \), and 2) at high temperatures and low \( P(\text{H}_2\text{O}) \), in an attempt to promote \( \text{Si(OH)}_4(g) \) and \( \text{SiO(OH)}_2(g) \) formation, respectively.
EXPERIMENTS & ANALYSIS

Apparatus

A schematic drawing of the transpiration cell together with the furnace, gas inlet and outlet systems are shown in figure 2. The transpiration cell (saturation chamber, inlet tube and collection tube) was made from Pt-20 wt%Rh to provide suitable high temperature strength. The inlet tube, walls and bottom end cap of the saturation chamber were laser-welded. The SiO$_2$ sample was loaded and sealed by welding the top end cap and outlet. The outlet consists of a 1mm diameter orifice, ~3mm OD and 10mm long, with the outside tapered to enable a gas tight seal with the collection tube. The whole unit was leak tested to ensure it was gas tight. The collection tube was swaged down to give a tight fit on the outside of the tapered exit orifice. Amorphous SiO$_2$ (99.99% pure, Quartz Scientific) was loaded into the saturation chamber in the form of porous frits, approximately 24mm in diameter and 4mm thick.

The temperature was measured at the center of the cell with a calibrated R-type thermocouple (Pt/Pt-13%Rh) that was inserted through the center of the inlet tube. In addition to temperature measurement, the thermocouple provided a restriction on the inlet side of the cell that effectively separates the inlet system and saturation chamber. Similarly the small diameter of the exit orifice separates the saturation chamber from the collection zone, limiting errors associated with diffusion transport.

The transpiration method can use either an inert or reactive carrier gas. This study used the combination of inert Ar (high purity, $O_2$ ~ 1 ppm) as the flowing media to which various amounts of reactive H$_2$O(g) were added. Ar was used instead of O$_2$(g) to reduce the formation of volatile platinum-oxide species and the possiblity of leaks forming in the cell. The pressure of the Ar was roughly controlled with a two-stage regulator and the flow rate controlled by a high-precision flow meter (Tylan General/Millipore). Liquid water was added directly to the flowing Ar. The flow rate of water, $Q_w$ (mole/sec), was accurately measured with a high-precision flow meter (Tylan General/Millipore).
controlled with a peristaltic pump (Rainin) and was measured before and after each experiment. To ensure entrainment of the water in Ar, prior to entering the furnace, the inlet tubing and water inlet were heated. After passing through the transpiration cell, the carrier gas cooled and the volume of condensed water was measured with a burette. The pressure of the Ar carrier gas was taken at point $l$ (in Fig. 2b). The cell was placed in the hot zone of a vertical tube furnace in an Al$_2$O$_3$ work tube. To ensure all the carrier gas was passed through the saturation chamber and collection tube during an experiment a blanket gas of flowing Ar (~60ml/min) was introduced into the Al$_2$O$_3$ work-tube, around the transpiration cell, and monitored for relative changes in the vapor species with a quadrupole mass spectrometer (Dycor). To ensure no water in the blanket gas condensed before reaching the mass spectrometer all tubing was heated.

Figure 2. a) Schematic of the transpiration cell and b) experimental setup.

The volatile Si-containing species in equilibrium with the condensed SiO$_2$ and carrier gas is transported from the saturation chamber through the exit orifice and condense out on the inner surface of the collection tube in a lower temperature region, located about 100-to-150mm above the saturation chamber. The number of moles of silicon containing molecules, $n_{Si}$ (assuming mono-silicon species, i.e., either Si(OH)$_4$(g), SiO(OH)$_2$(g) or SiO(OH)(g)) was determined by dissolving the condensate in 4% HF at 50°C and analyzing for silicon by plasma emission spectrometry. This data together with the time of the experiment was used to determine the molar flow rate of Si-containing vapor, $Q_{Si}$ (mole/sec).

Vapor pressure calculation

The vapor pressure of the Si-containing species in equilibrium with SiO$_2$ and the Ar + H$_2$O(g) carrier gas in the saturation chamber is calculated from the total number of moles of carrier gas that flow through the system and the number of moles of Si-containing species
measured in the collection tube for the duration of an experiment, assuming ideal behavior. The molar flow rate of Ar, $Q_{Ar}$ (mole/sec), is determined at point 1 (in Fig. 2b) from the measured room temperature $T_1$ (K), the total pressure, $P_1$ (atm), and the volume flow rate $f_1$ (ml/sec) according to equation [5].

$$Q_{Ar} = \frac{P_1 f_1}{RT_1}$$

The molar flow rate of H$_2$O(l) entering the system, $Q_{w}$, is controlled accurately and directly with the peristaltic pump, as discussed above. The total molar flow rate of vapor entering the saturation chamber (point 2) is given by $Q_2 = Q_{Ar} + Q_w$ and $Q_3 = Q_{Ar} + Q_w + Q_{Si}$ in the saturation chamber (point 3). As the molar flow rates of Ar and H$_2$O(g) are much larger then the Si-containing species, $Q_3 \approx Q_2$, and the volume flow rate in the saturation chamber, $f_3$, can be calculated according to equation [6] and the vapor pressure of the Si-containing vapor by equation [7].

$$f_3 = \frac{T_3}{P_3} R [Q_w + Q_{Ar}]$$

$$P_g = \frac{Q_g}{Q_{Ar} + Q_w + Q_{Si}} P_3 \text{ or } P_g = Q_g RT_3 / f_3$$

Ideally the total vapor pressure in the saturation chamber should be measured directly with a manometer (9,10). This was not necessary as the collection tube vents to the atmosphere the total vapor pressure in the saturation chamber was assumed to be equal to atmospheric pressure $P_j \equiv 1$ atm.

**Experimental Conditions**

The experiments in this study are divided into three parts. 1) In the setup procedure a suitable carrier gas flow rate is determined where equilibrium is obtained in the saturation chamber and diffusion transport is minimized. This involved a constant temperature ($T=1673 K$) and molar fraction of water ($X_{H_2O} \approx 0.33$) while varying the flow rate of the carrier gas ($f_3$ ranged between 80 and 140 ml/min). 2) Experiments which measure the vapor pressure of the Si-containing species as a function of reaction temperature. Initial experiments have focused on two different conditions, Ar carrier gas with mole fraction of water $X_{H_2O} \approx 0.37$ and $0.15$ at an average temperature of 1384 K and 1550 K, respectively. 3) Experiments varying the mole fraction of water in the carrier gas at 1187 K and 1722 K.

**RESULTS AND DISCUSSION**

**Flow Rate Determination**

The results of the flow rate determination are shown in Fig. 3 and indicate that the measured pressure of the Si-containing vapor is independent of the carrier gas flow rate, $f_3$, over the range spanning 10 to 24 ml/sec at 1673 K and $X_{H_2O} = 0.33$. The presence of such a plateau indicates the carrier gas has attained equilibrium with the condensed SiO$_2$ and there is almost no diffusion contribution to the transport of Si-vapor to the collection tube. The flow rate for all subsequent experiments was kept within these limits.
Condensed SiO₂ Phase

When the SiO₂ sample was sealed in the transpiration chamber it was amorphous. The SiO₂ transformed from the metastable amorphous phase to stable cristobalite as confirmed with room temperature x-ray diffraction analysis of a small portion of sample removed from the transpiration cell through the inlet tube after testing was completed. Comparison of the thermodynamic data (11,12) for cristobalite and amorphous SiO₂ show only a small difference in Gibbs energy of formation (2 kJ/mole) at the temperature range of interest, which is within the expected error of the measurements.

Species Identification

The molecular formula of the vapor species must be known to interpret the measured vapor pressure data. As discussed in the introduction, mass spectrometry has confirmed (3,6) the existence of three of the four Si-vapor species but only over a limited range of conditions. Therefore the transpiration method was used to identify Si-vapor species by considering the effect of varying \( X_{H₂O} \) on the pressure of Si-containing vapor. According to the equilibrium constants for equations [1]-[4] a slope of a plot of the logP(Si-OH) vs. logP(H₂O) should have the following values: 0.5, 1, 2, and 1.5 for SiO(OH)(g), SiO(OH)₂(g), Si(OH)₄(g) and Si₂O(OH)₆(g), respectively. SiO(OH)(g) should also show a dependence on the vapor pressure of O₂ while the others should be independent of O₂. According to the estimated data shown in Fig. 1 the dominant vapor species are expected to be SiO(OH)₂(g) and Si(OH)₄(g). The mole fraction of H₂O was varied at 1187 and 1722 K and the results are shown in Fig. 4. The pressure dependence of the Si-vapor with \( X_{H₂O} \) was determined to be 1.79±0.05 and 1.50±0.09 at 1187 and 1722 K, respectively. Both temperatures gave a slope between 1 and 2, indicating the vapor is a mixture of SiO(OH)₂(g) and Si(OH)₄(g) and both have similar pressures (as predicted by Krikorian’s data in Fig. 1). Such a dependence could also indicate Si₂O(OH)₆(g) but the current conditions are outside the 2000-to-9000 atm required (1) and no direct evidence for this species has been found.
Assuming the Si-containing vapor is a mixture of only SiO(OH)$_2$ + Si(OH)$_4$ and there is one mole of Si atoms in the vapor for each mole of SiO$_2$ consumed, the slopes of the P(H$_2$O) pressure dependence plots (in Fig. 4) can be used to predict the relative amounts of each species. Let $A$ and $B$ equal the fraction of SiO(OH)$_2$ and Si(OH)$_4$ in the Si-vapor, $A = P$(SiO(OH)$_2$)/$P$(Si-OH) and $B = P$(Si(OH)$_4$)/$P$(Si-OH), where $P$(Si-OH) is the measured pressure of the Si-containing vapor i.e., $A + B = 1$. Equations [2] and [3] can be rewritten and combined to give [8].

$$ASiO_2(s) + AH_2O(g) = A(Si - OH)(g)$$  \[2b\]

$$BSiO_2(s) + 2BH_2O(g) = B(Si - OH)(g)$$  \[3b\]

$$SiO_2(s) + (A + 2B)H_2O(g) = (Si - OH)(g)$$  \[8\]

The slope is, $d\log P$(Si-OH)/$d\log P$(H$_2$O) = $A + 2B$, and the fraction of each species at 1187 K is $A = 0.208$ and $B = 0.792$ and at 1722 K $A = 0.498$ and $B = 0.502$. This shows qualitative agreement with Krikorian’s predictions in Fig. 1, in that, Si(OH)$_4$ is dominant at lower temperatures and SiO(OH)$_2$ increases at higher pressures.

**Relevant Energy Determination**

At high temperatures ($> 1000$ K) and low vapor pressures ($\leq 1$ atm) Ar, H$_2$O(g) and Si-OH(g) are considered ideal and, assuming equilibrium, the equilibrium constant for
the reaction (e.g., equation [3]) is calculated from the measured partial pressures.

\[ K = \frac{P(Si(OH)_4)}{P(H_2O)^2} \]  

[9]

The standard free-energy change for the reaction at \( T \) is given by, \( \Delta G^o_r = -RT\ln K \), and the enthalpy and entropy of the reaction can be obtained, assuming \( \Delta C_p^o = 0 \), from the variation of \( \ln K \) with \( 1/T \) according to the "second law method":

\[ \ln K = \frac{-\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R} \]  

[10]

However, without clear identification of specific vapor species and accurate measurement of their pressures, the meaning of any measured thermodynamic data is ambiguous (6). At best, data determined from a complex vapor mixture, with the transpiration method, must be considered as a weighted-average of the reactions involved. From the above discussion, this is clearly an issue for the current measurements. It is unclear what reaction would best describe the formation of such a complex vapor but as the predicted fraction of \( Si(OH)_4(g) \) in the Si-vapor increases from 0.5 at 1722 K to about 0.8 at 1187 K the \( \ln K \) versus \( 1/T \) data was treated according to equation [3] and [9] (i.e., assuming \( Si(OH)_4 \)). This assumption also allows comparison to Hashimoto's results which assumed the same reaction. Two series of \( K \) measurements were made and are shown together with the data reported by Hashimoto in Fig. 5.

The data from both series show excellent agreement. Series 1 gave: \( \Delta H^o = 52.5 \pm 2.0 \) kJ/mole and \( \Delta S^o = -69.7 \pm 1.5 \) J/moleK at an average temperature of 1384 K, and series 2 gave: \( \Delta H^o = 52.9 \pm 3.7 \) kJ/mole and \( \Delta S^o = -68.6 \pm 2.5 \) J/moleK at an average temperature of

![Figure 5. \( \ln K \) versus \( 1/T \), assuming reaction [3], for: Series 1, \( T = 1384 \) K, \( X_{H_2O} = 0.37 \) (----) and Series 2, \( T = 1550 \) K, \( X_{H_2O} = 0.15 \) (----) together with the data from Hashimoto (----) (5).]
1550 K. These data also show good agreement with the data from Hashimoto (5) \( \Delta H^\circ = 56.7 \pm 1.7 \text{ kJ/mole} \) and \( \Delta S^\circ = -66.2 \pm 1.0 \text{ J/moleK} \) at an average temperature of 1600 K. Such a good agreement between the two indicate that the measured values of \( K \) are independent of \( X_{H_2O} \). It also strongly suggests Si(OH)\(_4\) is the dominant Si-vapor species over the experimental conditions in this study which agrees with Hashimoto. This is inconsistent with the results of varying \( X_{H_2O} \) which indicated the pressure of SiO(OH)\(_2\) was significant.

**SUMMARY & CONCLUSIONS**

This study is part of an ongoing effort to obtain reliable, experimentally determined thermodynamic data for silicon-oxyhydroxide and -hydroxide vapor species. The transpiration method was used to measure the pressure of Si-containing vapor in equilibrium with SiO\(_2\) (cristobalite) and an Ar + H\(_2\)O(g) mixture with various \( X_{H_2O} \) at temperatures ranging from 1000 to 1780 K. One of the major difficulties encountered in studying vapor species in the Si-O-H system is identifying the dominant vapor species. Thermochemical data found in the literature for this system differ on whether SiO(OH)\(_2\) is found at vapor pressures similar to Si(OH)\(_4\) over the experimental conditions of this study. Indeed, variation of \( X_{H_2O} \) at 1187 and 1722 K indicated the Si-containing vapor was probably a mixture of Si(OH)\(_4\) + SiO(OH)\(_2\). However this result is inconsistent with the statistically identical “second law” heats and entropies for Si(OH)\(_4\) formation from SiO\(_2\) and H\(_2\)O measured at different \( X_{H_2O} \) (0.15 and 0.37). In addition, the measured heats and entropies closely agreed with the available data for Si(OH)\(_4\) formation. Further pressure dependent studies are in progress to resolve these issues.

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**REFERENCES**