

THERMODYNAMICS OF SILICON-HYDROXIDE FORMATION IN H₂O CONTAINING ATMOSPHERES

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ABSTRACT

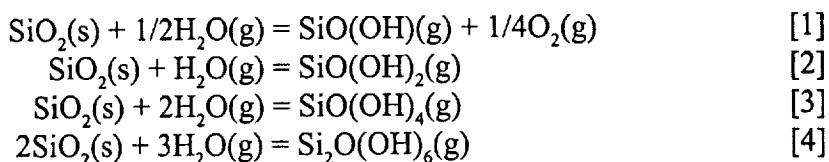
The formation of volatile silicon-hydroxide species from SiO₂ in water containing atmospheres has been identified as a potentially important mode of degradation of Si-based ceramics. Availability of thermodynamic data for these species is a major problem. This study is part of an ongoing effort to obtain 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, $X_{\text{H}_2\text{O}}$, at temperatures ranging from 1000 to 1780 K. Enthalpies and entropies for the reaction, $\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{g}) = \text{Si}(\text{OH})_4(\text{g})$, were obtained, at $X_{\text{H}_2\text{O}} = 0.15$ and 0.37 , from the variation of $\ln K$ with $1/T$ according to the "second law method". The following data were obtained: $\Delta H^\circ = 52.9 \pm 3.7$ kJ/mole and $\Delta S^\circ = -68.6 \pm 2.5$ J/moleK at an average temperature of 1550 K, and $\Delta H^\circ = 52.5 \pm 2.0$ kJ/mole and $\Delta S^\circ = -69.7 \pm 1.5$ J/moleK at an average temperature of 1384 K, for $X_{\text{H}_2\text{O}} = 0.15$ 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)(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 900 K 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 H₂O(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 Si(OH)₄(g) as the dominant vapor species at ~1770 K in a carrier gas consisting of 0.5 atm H₂O / balance O₂. The enthalpy and entropy of the reaction to form Si(OH)₄(g) from SiO₂ and H₂O(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 SiO₂(l) and H₂O(g) near 2000 K at P(H₂O) less than 5.0x10⁻⁵ atm. SiO(OH)(g) and 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 SiO₂ and H₂O(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 Si(OH)₄(g) and gave some evidence for SiO(OH)₂(g). There is no direct evidence for Si₂O(OH)₆(g).



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 Si(OH)₄. Clearly there is a large discrepancy between the two regarding the importance of SiO(OH)₂. If the data based on Krikorian estimates based data are considered, the dominant vapor species changes from Si(OH)₄(g) at low temperatures to 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(H₂O), and 2) at high temperatures and low P(H₂O), in an attempt to promote Si(OH)₄(g) and SiO(OH)₂(g) formation, respectively.

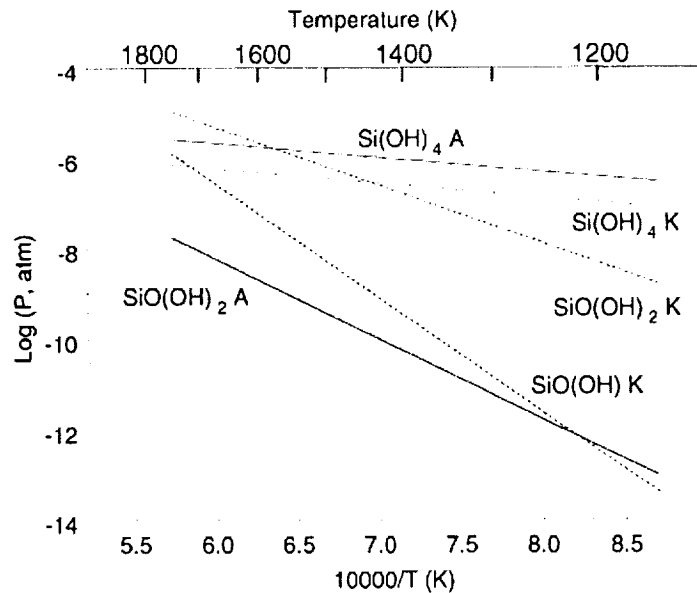


Figure 1. Estimated Si-OH vapor pressure over SiO_2 at $X_{\text{H}_2\text{O}} = 0.37$ at a total pressure of 1 atm.

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, $\text{O}_2 \sim 1$ ppm) as the flowing media to which various amounts of reactive $\text{H}_2\text{O}(\text{g})$ were added. Ar was used instead of $\text{O}_2(\text{g})$ to reduce the formation of volatile platinum-oxide species and the possibility 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 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].

$$Q_{Ar} = \frac{P_1 f_1}{RT_1} \quad [5]$$

The molar flow rate of $H_2O(l)$ 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 $H_2O(g)$ are much larger than the Si-containing species, $Q_3 \cong Q_2$, 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].

$$f_3 = \frac{T_3}{P_3} R [Q_w + Q_{Ar}] \quad [6]$$

$$P_{Si} = \frac{Q_{Si}}{Q_{Ar} + Q_w + Q_{Si}} \cdot P_3 \text{ or } P_{Si} = Q_{Si} RT_3 / f_3 \quad [7]$$

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 $P_3 \cong 1$ 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 ($T=1673K$) and molar fraction of water ($X_{H_2O} \sim 0.33$) while varying the flow rate of the carrier gas (f_1 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 $X_{H_2O} \cong 0.37$ 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.

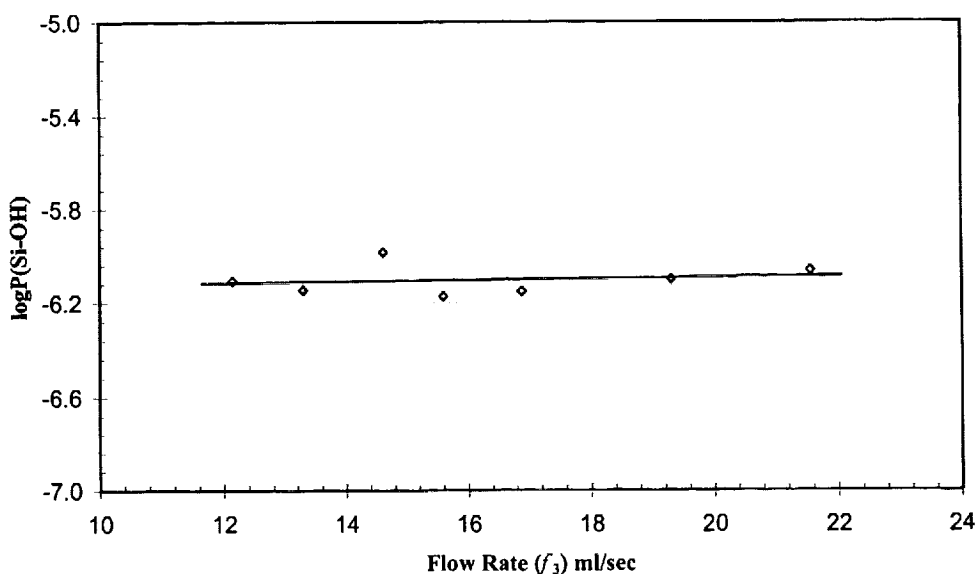


Figure 3. Variation of the pressure of Si-containing vapor with f_3 , measured at 1673 K and $X_{\text{H}_2\text{O}} = 0.33$.

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 $X_{\text{H}_2\text{O}}$ on the pressure of Si-containing vapor. According to the equilibrium constants for equations [1]-[4] a slope of a plot of the $\log P(\text{Si-OH})$ vs. $\log P(\text{H}_2\text{O})$ 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 $X_{\text{H}_2\text{O}}$ 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.

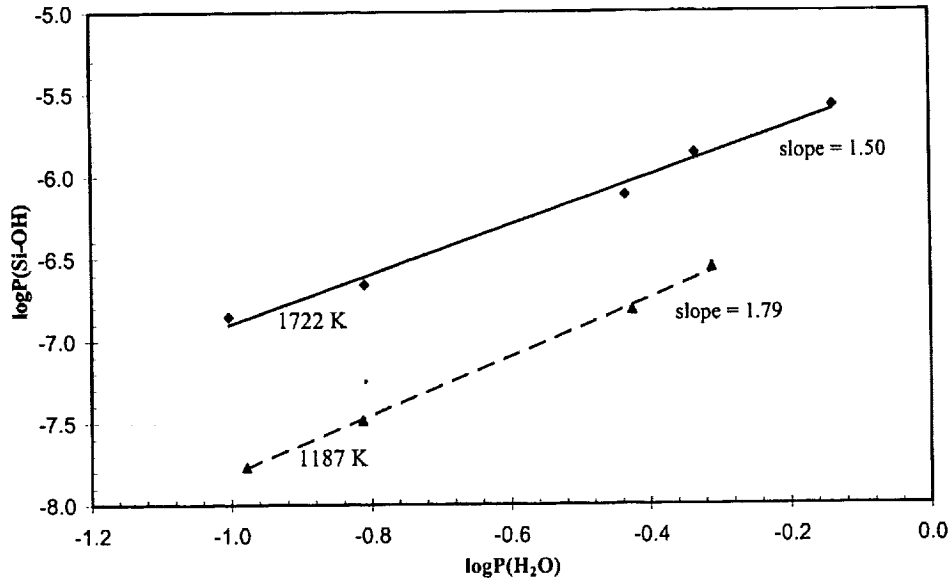
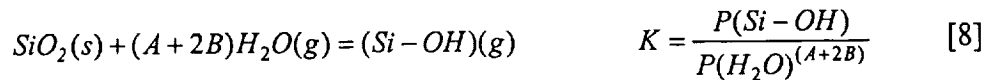
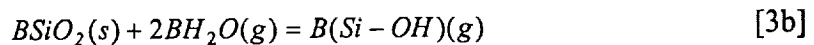
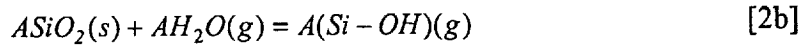


Figure 4. Effect of $X_{\text{H}_2\text{O}}$ -or $P(\text{H}_2\text{O})$ - on the total pressure of Si-containing vapor at 1187 and 1722 K, assuming Si-vapor species contain only one atom of Si per molecule.

These results are in variance with Hashimoto (5) and Allendorf's *et al.* calculations (7) which clearly show $\text{Si}(\text{OH})_4(\text{g})$ is the dominant Si-containing species. The major difference between the current experiments and those of Hashimoto is the composition of the carrier gas. This study used $\text{H}_2\text{O}(\text{g})$ in flowing Ar while Hashimoto used a $\text{H}_2\text{O}(\text{g})+\text{O}_2$ mixture. This difference suggests the pressure of Si-vapor is a function of the $P(\text{H}_2\text{O})/P(\text{O}_2)$ ratio. This goes against our current understanding of the Si-O-H system and needs further investigation with a range of Ar+ $\text{H}_2\text{O}(\text{g})+\text{O}_2$ carrier gas mixtures over a range of temperatures.

Assuming the Si-containing vapor is a mixture of only $\text{SiO}(\text{OH})_2 + \text{Si}(\text{OH})_4$ and there is one mole of Si atoms in the vapor for each mole of SiO_2 consumed, the slopes of the $P(\text{H}_2\text{O})$ 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 $\text{SiO}(\text{OH})_2$ and $\text{Si}(\text{OH})_4$ in the Si-vapor, $A = P(\text{SiO}(\text{OH})_2)/P(\text{Si-OH})$ and $B = P(\text{Si}(\text{OH})_4)/P(\text{Si-OH})$, where $P(\text{Si-OH})$ 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].



The slope is, $d\log P(\text{Si-OH})/d\log P(\text{H}_2\text{O}) = A+2B$, 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, $\text{Si}(\text{OH})_4$ is dominant at lower temperatures and $\text{SiO}(\text{OH})_2$ increases at higher pressures.

Reaction Energy Determination

At high temperatures (> 1000 K) and low vapor pressures (≤ 1 atm) Ar, $\text{H}_2\text{O}(\text{g})$ 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.

$$K = \frac{P(\text{Si}(\text{OH})_4)}{P(\text{H}_2\text{O})^2} \quad [9]$$

The standard free-energy change for the reaction at T_3 is given by, $\Delta G^\circ = -RT \ln K$, and the enthalpy and entropy of the reaction can be obtained, assuming $\Delta C_p^\circ = 0$, from the variation of $\ln K$ with $1/T$ according to the "second law method":

$$\ln K = \frac{-\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad [10]$$

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 $\text{Si}(\text{OH})_4(\text{g})$ 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 $\text{Si}(\text{OH})_4$). 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: $\Delta H^\circ = 52.5 \pm 2.0$ kJ/mole and $\Delta S^\circ = -69.7 \pm 1.5$ J/moleK at an average temperature of 1384 K, and series 2 gave: $\Delta H^\circ = 52.9 \pm 3.7$ kJ/mole and $\Delta S^\circ = -68.6 \pm 2.5$ J/moleK at an average temperature of

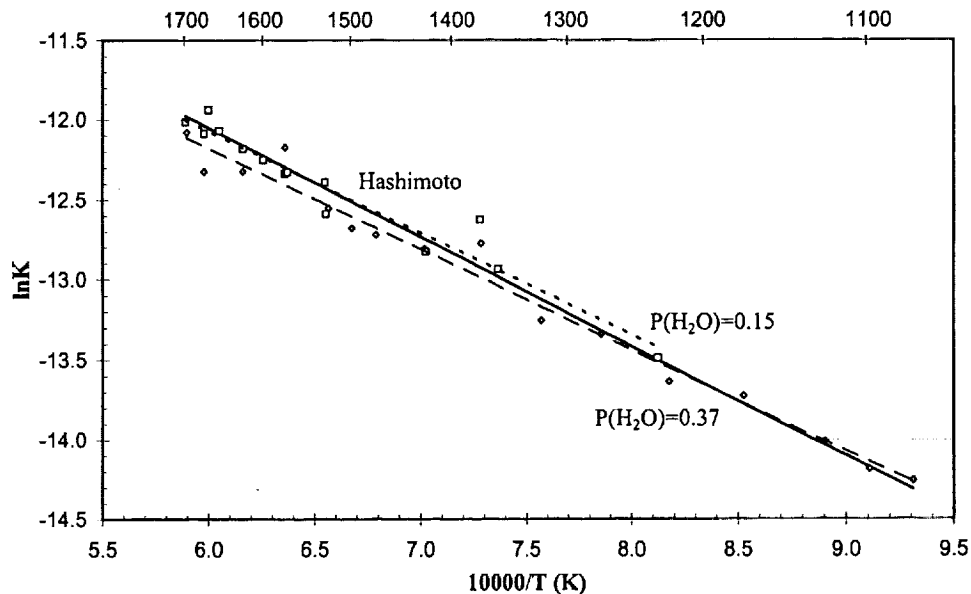


Figure 5. $\ln K$ versus $1/T$, assuming reaction [3], for: **Series 1**, $T = 1384$ K, $X_{\text{H}_2\text{O}} = 0.37$ (----) and **Series 2**, $T = 1550$ K, $X_{\text{H}_2\text{O}} = 0.15$ (—) together with the data from Hashimoto (—) (5).

1550 K. These data also show good agreement with the data from Hashimoto (5) $\Delta H^\circ = 56.7 \pm 1.7$ kJ/mole and $\Delta S^\circ = -66.2 \pm 1.0$ 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 $\text{Si}(\text{OH})_4$ 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 $\text{SiO}(\text{OH})_2$ 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 + $\text{H}_2\text{O}(\text{g})$ 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 $\text{SiO}(\text{OH})_2$ is found at vapor pressures similar to $\text{Si}(\text{OH})_4$ 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 $\text{Si}(\text{OH})_4$ + $\text{SiO}(\text{OH})_2$. However this result is inconsistent with the statistically identical "second law" heats and entropies for $\text{Si}(\text{OH})_4$ formation from SiO_2 and H_2O 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 $\text{Si}(\text{OH})_4$ formation. Further pressure dependent studies are in progress to resolve these issues.

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REFERENCES

1. O. H. Krikorian, in *Symposium on Engineering with Nuclear Explosives* (Las Vegas, NV, Jan 14-16, 1970), vol 1, unpublished.
2. E. J. Opila, N. S. Jacobson, *Electrochemical Society Proceedings*, vol 96-26, 269, (1996).
3. E. J. Opila, D. S. Fox, N. S. Jacobson, *J. Am. Ceram. Soc.*, 80, [4], 1009 (1997).
4. E. J. Opila, J. Smialek, C. Robinson, D. S. Fox, N. S. Jacobson, *J. Am. Ceram. Soc.*, 82, [7], 1826 (1999).
5. A. Hashimoto, *Geochim. Cosmochim. Acta*, 56, 511, (1992).
6. D. L. Hildenbrand, K. H. Lau, *J. Chem. Phys.* 101 [7] 6076, (1994).
7. M. D. Allendorf, C. F. Melius, P. Ho, M. R. Zachariah, *J. Phys. Chem.* 99, 15285, (1995).
8. G. Eriksson, K. Hack, *Metallurgical Transactions B*, vol 21B, 1013, (1990).
9. U. Merten, W. E. Bell, *The Transpiration Method, Chapter 4 in The Characterisation of High Temperature Vapors*, J. L. Margrave, ed., John Wiley & Sons, New York, 1967.
10. J. H. Norman, P. Winchell, *Measurement of Vapor Pressures by Transpiration, Isopiestic, and other Techniques, Chapter 2C in Techniques of Materials Research Vol. IV Physicochemical Measurements in Materials Research*, R. A. Rapp, ed., Interscience Publishers, New York, 1970.
11. A. Navrotsky, *Rev. Mineral.* 29, 309, 1994.
12. M. W. Chase, *NIST-JANAF Thermochemical Tables*, American Chemical Society and American Physical Society, New York, 1998.