Summary

Thermodynamic functions for Si(OH)$_4$(g) and SiO(OH)$_2$(g) have been measured using the transpiration method. A second law enthalpy of formation and entropy and a third law enthalpy of formation has been calculated for Si(OH)$_4$. The results are in very good agreement with previous experimental measurements, ab-initio calculations, and estimates.
Thermodynamics of the Si-O-H System
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Introduction

Silicon-oxygen-hydrogen gas phase species are important in a variety of applications, including high temperature corrosion of SiO$_2$ forming alloys and ceramics in water vapor containing environments.$^{1-3}$ Measurements of the pressures of Si-O-H species have been made using a transpiration apparatus similar to the design of Hashimoto.$^{4,11}$ The system can be used to provide flowing atmospheres of oxygen or argon with variable partial pressures of water. Samples of SiO$_2$ were placed in a Pt-20%Rh cell and heated from 900-1450°C. Volatile silicon hydroxides were transported by gas flow to the cooler condenser tube connected to the outlet nozzle and collected for chemical analysis.

Previous studies suggest the following reactions are important in the formation of silicon hydroxides and oxy-hydroxides:$^{5-9}$

$$\text{SiO}_2(\text{s}) + \frac{1}{2} \text{H}_2\text{O}(\text{g}) = \text{SiO(OH)}(\text{g}) + \frac{1}{4} \text{O}_2(\text{g})$$  \hspace{0.5cm} (1a)
$$\text{SiO}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{SiO(OH)}_2(\text{g})$$  \hspace{0.5cm} (1b)
$$\text{SiO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) = \text{Si(OH)}_4(\text{g})$$  \hspace{0.5cm} (1c)
$$2 \text{SiO}_2(\text{s}) + 3 \text{H}_2\text{O}(\text{g}) = \text{Si}_2\text{O(OH)}_6(\text{g})$$  \hspace{0.5cm} (1d)

Allendorf et al.$^{6,7}$ report theoretical heats of formation at 298.15 K and Gibbs free energies of formation for a range of Si-O-H gaseous species. Free-jet expansion sampling mass spectrometry was used to study the interactions of SiO$_2$ with water vapor.$^{10}$ Clear evidence of Si(OH)$_4$(g) as well as some evidence of SiO(OH)$_2$(g) was seen.
Figure 1. Schematic of transpiration apparatus
Flow and Pressure Calculations

The amount of Si containing condensate was converted to pressures by considering the flow rate of the argon carrier gas, water vapor, and the Si vapor species. Consider first the molar flow rate of Ar, $Q_{Ar}$, entering the furnace (Figure 1, point 1) before water is introduced:

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

Here $P_1$ is the pressure, $f_1$ is the volume flow rate, $R$ is the gas constant, and $T_1$ is the absolute temperature. The volume flow rate entering the reaction chamber (point 2) is given by

$$f_2 = \frac{T_2}{P_2} R [Q_W + Q_{Ar}]$$

Here $Q_W$ is the molar flow rate of water. The volume flow rate leaving the reaction chamber (point 3) is the above expression with the addition of $Q_{Si}$, which is small in comparison to $Q_W + Q_{Ar}$, so we can take $f_3 = f_2$. The pressure of Si-containing species leaving the reaction chamber (point 3) is given by:

$$\frac{P_{Si}}{P_T} = \frac{Q_{Si}}{Q_{Ar} + Q_W + Q_{Si}}$$

or

$$\frac{P_{Si}}{P_T} = \frac{Q_{Si} RT_3}{f_3}$$
Figure 2. Dependence of the Si-O-H species pressure on $P(\text{H}_2\text{O})$.

$P(\text{H}_2\text{O})$ dependence $< 2$ at higher temperatures suggests an additional reaction besides 1c is important at these temperatures.
Figure 3. Effect of oxygen on P(Si-OH) at 1673 K.

Lack of P(O_2) dependence indicates reaction 1a is not important.
Figure 4. Temperature dependence below 1673 K for the reaction
\[ \text{SiO}_2(s) + 2\text{H}_2\text{O}(g) = \text{Si(OH)}_4(g) \]

\[ \Delta H = 54.6 \pm 2.7 \]
\[ \Delta S = -67.5 \pm 2.1 \]
The calculations of Allendorf et al.\textsuperscript{6,7} allow the derivation of the free energy function for a third law calculation of $\Delta_t H^o(298)$. Their thermal functions listed on the Web\textsuperscript{7} can be used to extract the change in free energy function for the formation of Si(OH)$_4$ or $\Delta_t FEF^o(298)$. Using JANAF\textsuperscript{12} data for Si, O$_2$, and H$_2$ the FEF(Si(OH)$_4$) is determined to be:

$$FEF \ ( Si \ ( OH \ )_4 ) = 291.214 - 0.056846T + (6.6727 \times 10^{-6})T^2 - 32123.721/T - 89.8145 \ ln(T)$$

This was used with the standard third law equation to calculate an enthalpy of reaction for reaction (1c):

$$\Delta_r H^o(298) = \Delta G^o(T) - T \Delta \left(\frac{G^o(T) - H^o(298)}{T}\right) = RT \ln K_p - T \Delta (FEF^o(298))$$

See Table I for calculated enthalpies.
Table I. Calculated enthalpies of formation and entropies of Si(OH)$_4$(g)

<table>
<thead>
<tr>
<th>Method</th>
<th>Investigator</th>
<th>$\Delta_h$(1200) (kJ/mol)</th>
<th>$S^\circ$(1200) (J/mol-K)</th>
<th>$\Delta_h$(1600) (kJ/mol)</th>
<th>$S^\circ$(1600) (J/mol-K)</th>
<th>$\Delta_h$(298) (kJ/mol)</th>
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<tr>
<td>Second Law</td>
<td>Hashimoto$^4$</td>
<td>-1354 ± 2.7</td>
<td>544.1 ± 2.1</td>
<td>-1342.7 ± 2.7</td>
<td>592.5 ± 1.0</td>
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<tr>
<td>Second Law</td>
<td>This study</td>
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<tr>
<td>Third Law</td>
<td>Hashimoto$^{4,*}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1344.1 ± 0.3</td>
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<td>-1344.1 ± 1.4</td>
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<td>Estimation</td>
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<td>511</td>
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<td>ab-initio Calculations</td>
<td>Allendorf et al.$^{6,7}$</td>
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<td>539.47</td>
<td>-1339.9</td>
<td>587.21</td>
<td>-1342</td>
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</table>

$^*$FEF from Allendorf et al.$^{6,7}$
Figure 5. Pressures of SiO(OH)$_2$ at 1673 K.

\[ P(\text{Si-OH})^{\text{total}} - P(\text{Si(OH)}_4)^{\text{extrap}} \]

\[ P(\text{Si-OH})^{\text{total}} \]

\[ P(\text{Si(OH)}_4)^{\text{extrap}} \]

\[ P(\text{SiO(OH)}_2) \]

Slope = 0.79 +/- 0.23

\[ P(\text{H}_2\text{O}) \]
Figure 6. Pressures of SiO(OH)$_2$ at 1728 K.
The calculations of Allendorf et al.\textsuperscript{6,7} were also used to calculate FEF(SiO(OH)\textsubscript{2}). Using JANAF\textsuperscript{12} data for Si, O\textsubscript{2}, and H\textsubscript{2} the FEF(SiO(OH)\textsubscript{2}) is determined to be:

\[
FEF\ (SiO\ (OH)\textsubscript{2}) = 141.54 - 0.039543T + (4.3293 \times 10^{-6})T^2
- 21602T - 61.809 \ ln(T)
\]

See Table II for calculated third law enthalpies.
Table II. Enthalpy of formation of SiO(OH)$_2$ from this study and other studies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Investigator</th>
<th>Thermal Functions</th>
<th>$\Delta_f H^\circ(298)$</th>
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<tr>
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<td>Hildenbrand and Lau</td>
<td>Estimated</td>
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<td>Hildenbrand and Lau</td>
<td>Allendorf et al.</td>
<td>-811 ± 18</td>
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<tr>
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<td>Allendorf et al.</td>
<td>-755.7</td>
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<td>Transpiration</td>
<td>This study</td>
<td>Allendorf et al.</td>
<td>-831 ± 5.1</td>
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</table>
Summary and Conclusions

Thermodynamic functions for Si(OH)$_4$(g) and SiO(OH)$_2$(g) have been measured using the transpiration method. A second law enthalpy of formation and entropy and a third law enthalpy of formation has been calculated for Si(OH)$_4$. The results are in very good agreement with previous experimental measurements, \textit{ab-initio} calculations, and estimates.

At temperatures of 1673 and 1728 K, water vapor pressure dependent experiments suggest that a second vapor species is important. Lack of oxygen dependence suggests this species is SiO(OH)$_2$. By subtracting the extrapolated pressure of Si(OH)$_4$(g) at 1673 and 1728 K, pressures of SiO(OH)$_2$(g) are determined. These values were used in a third law analysis to obtain a heat of formation of SiO(OH)$_2$. Recalculation of gas-leak Knudsen cell third law data from Hildenbrand and Lau$^{8,9}$ using the thermal functions of Allendorf \textit{et al.}$^{6,7}$ leads to a heat of formation of SiO(OH)$_2$ in reasonable agreement with the transpiration data of this study.

Acknowledgements

Dan Simon and Greg Blank - design and construction of transpiration cell
Derek Johnson - silicon analysis