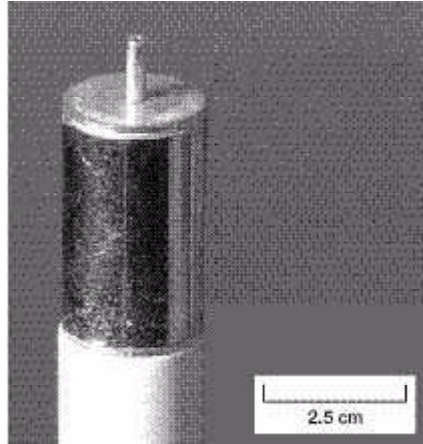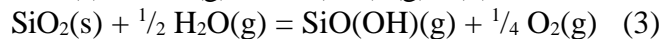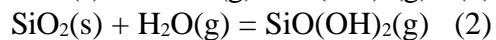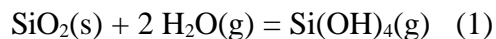# Thermodynamics of Volatile Silicon Hydroxides Studied

Pt-Rh transpiration cell.

Silicon-based ceramics are promising candidate structural materials for heat engines. The long-term stability of these materials to environmental degradation is dependent on the formation and retention of a protective SiO_2 layer. It is well known that SiO_2 forms stable volatile hydroxides in the presence of water vapor at elevated temperatures. Combustion conditions, which characteristically are at high velocities, contain significant water vapor pressures, and high temperatures tend to promote continuous formation of these hydroxides with resulting material degradation. For the degradation of silicon-based ceramics to be predicted, accurate thermodynamic data on the formation of silicon hydroxides are needed.

Three volatile silicon-hydroxide species have been proposed as being significant under combustion conditions:

$$SiO_2(s) + 2\ H_2O(g) = Si(OH)_4(g) \quad (1)$$
$$SiO_2(s) + H_2O(g) = SiO(OH)_2(g) \quad (2)$$
$$SiO_2(s) + \tfrac{1}{2}\ H_2O(g) = SiO(OH)(g) + \tfrac{1}{4}\ O_2(g) \quad (3)$$

Thermodynamic data on these species are limited (refs. 1 to 5). A transpiration apparatus was designed and constructed to measure thermodynamic quantities for these volatile hydroxides and add to the available data.

Volatile hydroxides are formed by flowing a carrier gas containing a controlled amount of water vapor over solid SiO_2 at temperatures above 800 °C. The volatile species leave the transpiration cell, condense downstream on a cool collection tube, and are analyzed. Temperature, carrier gas flow rate, and water vapor pressure must be carefully controlled to ensure that equilibrium is obtained within the cell, to minimize diffusion effects, and to completely collect the reaction products. The transpiration cell, which was based on a design of Hashimoto (ref. 1), was fabricated at Glenn from Pt-20%Rh (see the figure). Laser welding was used to ensure a leak-tight system. The cell can be used with both

reactive and nonreactive carrier gases at temperatures up to 1773 K.

Initial studies at the NASA Glenn Research Center focused on experiments with an argon carrier gas containing high- (0.38-atm) and low- (0.15-atm) pressure water ($P(H_2O)$) flowing over amorphous SiO_2. The first series at high $P(H_2O)$ was conducted at temperatures between 1073 and 1723 K and, according to reaction (1), gave $\Delta H_r = 49.8\pm1.8$ kJ/mole and $\Delta S_r = -72.6\pm1.3$ J/mole. The second series of measurements at lower $P(H_2O)$ were taken over the temperature range of 1450 to 1723 K. According to reaction (1), these results gave $\Delta H_r = 56.9\pm0.8$ kJ/mole and $\Delta S_r = 66.9\pm0.5$J/mole. The results show excellent agreement with recent data from Hashimoto (ref. 1) for the formation of $Si(OH)_4(g)$: $\Delta H_r = 56.7\pm1.7$ kJ/mole and $\Delta S_r = -66.2\pm1.0$ J/mole at an average temperature of 1600 K. The difference between the two data sets suggests $SiO(OH)_2(g)$ may be forming. Further work is underway to clarify this and obtain data for $SiO(OH)_2(g)$.

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