

1N-27
372 708

VOLATILE Si-O-H SPECIES IN COMBUSTION ENVIRONMENTS

Elizabeth J. Opila
Cleveland State University
Cleveland, OH 44115

Nathan S. Jacobson
NASA Lewis Research Center
Cleveland, OH 44135

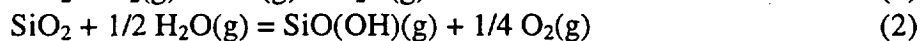
The formation of volatile Si-O-H species from silica occurs in water-vapor containing environments such as combustion environments. In this paper the pressure and temperature dependence of known Si-O-H species are surveyed. Trends based on the number of water molecules incorporated in the Si-O-H species are identified. Larger molecules (more OH groups) tend to have a higher pressure dependence and lower temperature dependence. These trends are then used to identify possible unknown species observed in high pressure fuel-rich combustion environments.

INTRODUCTION

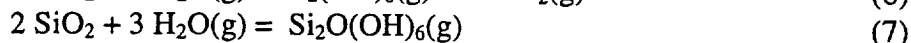
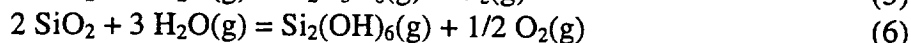
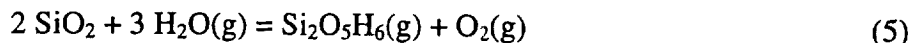
Silica protected ceramics are proposed for use in combustion environments. The combustion of hydrocarbon fuels and air produces gaseous products composed of about ten percent water vapor independent of the fuel to air ratio [1]. The reaction of water vapor with silica is known to form volatile Si-O-H species. In this paper the formation of volatile Si-O-H species in combustion environments of varying pressures and gas chemistries is discussed.

Silica volatility has been demonstrated by thermogravimetric measurements of silica exposed to 50% H₂O/50% O₂ in a controlled furnace environment [2]. In addition silica volatility from oxidizing SiC in a High Pressure Burner Rig (HPBR) has been shown by interrupted weight change measurements in both fuel-lean and fuel-rich environments [3]. Examples of these weight losses are shown in Figure 1.

Many volatile silicon oxide, hydroxide, and oxyhydroxide species have been observed or proposed to exist. The formation reactions for those which have been observed are as follows:



In addition, several SiO₂ volatilization reactions may occur under high pressure conditions:



When the volatile species are known, measured volatility rates show good agreement with rates calculated based on a gaseous boundary layer controlled process. The flux of volatile species, J, through a gaseous boundary layer under laminar flow conditions is given by:

$$J = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3} \frac{D\rho}{L} \quad (8)$$

$$J = 0.664 \left(\frac{\rho' vL}{\eta} \right)^{1/2} \left(\frac{\eta}{\rho' D} \right)^{1/3} \frac{D\rho}{L} \quad (9)$$

where Re is the Reynold's number of the boundary layer gas, Sc is the Schmidt number of the boundary layer gas, ρ' is the boundary layer gas density, v is the linear gas velocity, L is a characteristic length of the sample, η is the gas viscosity, D is the interdiffusion coefficient of the volatile species in the boundary layer, and ρ is the gas density of the volatile species. D is proportional to the inverse of the total pressure, ρ' is proportional to the total pressure, and ρ is proportional to the partial pressure of the volatile species. The pressure dependence of the flux is thus:

$$J \propto \frac{P_{\text{Si-O-H}}}{P_{\text{total}}^{1/2}} \quad (10)$$

The temperature dependence of the flux is primarily determined from the formation enthalpy of the volatile species from SiO₂ and water vapor by reactions 1 through 7.

PROCEDURE

In this paper, the pressure conditions under which known Si-O-H species have been observed are surveyed. The dependence of the flux on total pressure for each volatile silica species is evaluated based on Equations 8 through 10. The temperature dependence of the flux of each known volatile species is then surveyed. The formation enthalpy of

the volatile species formed in reactions 1 through 7 are then ranked based on entropy arguments. Finally, these trends are used to identify possible unknown species observed in high pressure fuel-rich combustion environments.

RESULTS AND DISCUSSION

Low Pressure

Mass spectrometric Knudsen Cell studies provide limited data for the formation of SiO(OH) and SiO(OH)_2 [4] from SiO_2 in low partial pressures of H_2O . In addition, estimated data for SiO(OH) [5,6,7] and SiO(OH)_2 [5,6] are available.

Atmospheric Pressure

Thermochemical data for the formation of Si(OH)_4 from SiO_2 in oxygen/water vapor mixtures at atmospheric pressure have been measured by a transpiration technique [8]. The formation of this volatile species has been confirmed by specialized sampling mass spectrometer [9]. Evidence for formation of small amounts of SiO(OH)_2 was also found under these conditions [9]. Estimated data for Si(OH)_4 are also available from several sources [5,6]. In roughly 4% H_2 / 12% H_2O mixtures in nitrogen, hydroxide formation is not observed: instead, SiO appears to be the primary volatile species [10].

High Pressure

Si(OH)_4 is again the primary volatile species from SiO_2 in $\text{O}_2/\text{H}_2\text{O}$ containing mixtures at pressures in the range of 10 atm [11]. $\text{Si}_2\text{O(OH)}_6$ is thought to be important at very high pressures (~100 atm), though it has never been confirmed [6]. High pressure $\text{H}_2/\text{H}_2\text{O}$ containing mixtures (~10 atm) result in formation of yet unidentified Si-O-H species; $\text{Si}_2(\text{OH})_6$ or $\text{Si}_2\text{O}_5\text{H}_6$ may explain some of the observations [11]. In high pressure oxidizing environments, traditional mass spectrometric techniques can not be used and indirect methods, such as examination of the pressure and temperature dependences of volatilization, are necessary.

Pressure Effects

Volatile species increase in complexity as the total combustion gas pressure increases. At higher pressures, more water molecules react with silica to form larger Si-O-H molecules. The partial pressures of more complex volatile species have a larger dependence on the water vapor partial pressure as shown in Figure 2. Since the water vapor and oxygen partial pressures scale with the total pressure in combustion environments, the partial pressure of volatile species can be related to the total pressure in the combustion environment. Using Si(OH)_4 as an example: From Reaction 4 we know

that $P(\text{Si}(\text{OH})_4) \propto P(\text{H}_2\text{O})^2 \propto (P_{\text{total}})^2$. Assuming laminar flow and using Equation 10, then, $J(\text{Si}(\text{OH})_4) \propto (P_{\text{total}})^{3/2}$. These relationships have been summarized in Table 1 for the volatile species formed in Reactions 1 through 7.

Table 1. Pressure dependence for Si-O-H Formation

Species	$P(\text{Si-O-H}) \propto (P_{\text{total}})^n$	$J(\text{Si-O-H}) \propto (P_{\text{total}})^m$
SiO	n=0	m=-0.5
SiO(OH)	n=0.25	m=-0.25
SiO(OH) ₂	n=1	m=0.5
Si(OH) ₄	n=2	m=1.5
Si ₂ O ₅ H ₆	n=2	m=1.5
Si ₂ (OH) ₆	n=2.5	m=2
Si ₂ O(OH) ₆	n=3	m=2.5

Temperature Effects

All known values for the enthalpy of formation of volatile Si-O-H species from SiO₂ and H₂O, both estimated and measured, are summarized in Table 2.

Table 2
Temperature Dependence of Si-O-H(g) Species,
Reaction Enthalpy for SiO₂ + H₂O = Si-O-H(g) at 1600K

Species	Source for Thermochemical Data	Reaction Enthalpy, kJ/mol
SiO(OH)	Hildenbrand*	530
	Hildenbrand revised*	670
	Krikorian	524
	Allendorf	713
	Darling & Schlegel	721
SiO(OH) ₂	Hildenbrand*	260
	Krikorian	247
	Allendorf	346
Si(OH) ₄	Hashimoto*	57
	Krikorian	32
	Allendorf	60
Si ₂ O(OH) ₆	Krikorian	-49

*experimentally determined, all others estimated or calculated

It is interesting to note that as the complexity of the molecule increases the formation enthalpy decreases.

This trend can be understood by considering the entropy of reaction. Following the approach of Searcy [12], it can be seen that the entropy of reaction is positive for those reactions which result in a net increase of gas molecules and negative for those reactions where there is a net decrease in number of gas molecules. The net change in number of gas molecules per mole of silica for each volatile Si-O-H species is shown in Table 3.

Table 3. Change in # of gas molecules for reactions of the type

$\text{SiO}_2 + \text{H}_2\text{O}(\text{g}) = \text{Si-O-H}(\text{g}) + \text{O}_2(\text{g})$	
Volatile Species	change in # of gas molecules/# SiO_2
SiO(OH)	+3/4
SiO(OH) ₂	0
Si ₂ O ₃ H ₆	-1/2
Si ₂ (OH) ₆	-3/4
Si(OH) ₄	-1
Si ₂ O(OH) ₆	-1

Some estimate of the formation enthalpy can now be made by equating two formulations of the free energy of reaction:

$$\Delta H - T\Delta S = -RT \ln K \quad (11)$$

For a given free energy of reaction, those reactions with the most positive entropy of reaction will have a high enthalpy of reaction. Similarly, those reactions with a net loss of entropy will have very small enthalpies of reaction. The small molecules therefore have high temperature dependence while the larger molecules are only weakly temperature dependent. This has been verified experimentally. For example, SiO(OH) formation (Reaction 2) has been found to have an enthalpy of reaction of 670 kJ/mol [4], while Si(OH)₄ formation (Reaction 4) has been found to have an enthalpy of reaction at 1600K of 56.7 kJ/mol [8]. In actuality, the formation enthalpies do not have a strict negative correlation with the number of gas molecules created or destroyed since the equilibrium constant K depends on $P(\text{H}_2\text{O})^n$ in some cases and in other cases $P(\text{O}_2)^m$ and $P(\text{H}_2\text{O})^n$ where n and m vary.

For the purposes of this report, we are interested in the volatile species present in the high pressure fuel-rich environment, as will be discussed in the next section. Given these conditions, the enthalpies of formation of the volatile species (Reactions 2 through 7) can be estimated using the following assumptions. First, it is known that the entropy change for reaction 4 is -66 eu [8]. This value can be used as a rough estimate for the entropy change to lose one gas molecule in these types of reactions. Second, we assume that the partial pressure of the volatile Si-O-H species is 10^{-6} atm which is a reasonable value for

a lower limit at which volatility can be observed by weight change measurements in typical experimental times. Next, it is assumed that the chemistry of the combustion environment is described by $P(\text{total}) = 6.3 \text{ atm}$, $P(\text{H}_2\text{O}) = 0.63 \text{ atm}$, $P(\text{O}_2) = 1 \times 10^{-7} \text{ atm}$. These partial pressure conditions are present in the HPBR experiments of interest. Given these three assumptions, values for ΔS and $\ln K$ can be inserted in Equation 11 and ΔH can in turn be estimated. The first two assumptions may not be accurate, so that the formation enthalpies estimated here are not reported numerically, but ranked, in Table 4, and compared to literature values where available. The formation enthalpy of $\text{Si}_2(\text{OH})_6$ was found to be quite similar to that of $\text{Si}(\text{OH})_4$ while that of $\text{Si}_2\text{O}_5\text{H}_6$ was midway between $\text{SiO}(\text{OH})_2$ and $\text{Si}(\text{OH})_4$.

Table 4. Estimated magnitude of Formation Enthalpy for Volatile Si-O-H Species

Volatile Si-O-H Species	Estimated Formation Enthalpy	Average Value for Enthalpy Reported in Literature (kJ/mol)
$\text{SiO}(\text{OH})$	largest	630
$\text{SiO}(\text{OH})_2$	↓	284
$\text{Si}_2\text{O}_5\text{H}_6$		--
$\text{Si}_2(\text{OH})_6$		--
$\text{Si}(\text{OH})_4$		50
$\text{Si}_2\text{O}(\text{OH})_6$		smallest

Combustion Gas Chemistry Effects

Robinson et al. [3] found that silica volatility varies in the combustion environment of a high pressure burner rig as the fuel to air ratio is varied. This is shown graphically in Figure 3. While flow in the burner rig is turbulent, flow along the length of the flat plate burner rig specimens is laminar due to the limited sample size. Laminar flow has been verified in the high pressure burner rig under fuel-lean conditions since the magnitude, pressure dependence, temperature dependence and velocity of the flux of volatile Si-O-H species are modeled quite well by assuming $\text{Si}(\text{OH})_4$ formation, laminar flow, and by using Equation 9 [11]. Volatility rates are substantially larger in the fuel-rich $\text{H}_2/\text{H}_2\text{O}$ containing environments compared to $\text{O}_2/\text{H}_2\text{O}$ environments when gas pressure, velocity, temperature and H_2O content are held constant. This result may be explained by the formation of additional volatile species in $\text{H}_2/\text{H}_2\text{O}$ environments. From above, it can be seen that volatile species formed by Reactions 3, 4, and 7 should depend only on H_2O content and therefore can not explain these results. Reactions such as 2, 5 and 6 which form oxygen as a product would more likely explain the increased volatility observed in $\text{H}_2/\text{H}_2\text{O}$ containing environments.

Attempts were made to identify any possible formation of additional volatile Si-O-H species based on the following assumptions. It was assumed that Si(OH)_4 is present in the fuel-rich environment in amounts predicted from the data of Hashimoto [8] and Equation 9. It was further assumed that the additional volatility could be attributed to the formation of a single additional species. Therefore, the calculated flux of Si(OH)_4 was subtracted from the experimentally determined flux in the fuel-rich environment. The pressure dependence of this additional flux was found to have a power law exponent of 2 as shown in Figure 4. This result is consistent with the formation of $\text{Si}_2(\text{OH})_6$. In the same way, the temperature dependence of the flux not attributed to Si(OH)_4 or SiO was found to have a formation enthalpy of 170 kJ/mol as shown in Figure 5. This is most consistent with $\text{Si}_2\text{O}_5\text{H}_6$ formation. Both $\text{Si}_2(\text{OH})_6$ and $\text{Si}_2\text{O}_5\text{H}_6$ are consistent with the low $\text{P(O}_2)$ environment.

The next step in identifying if either of these species is important in fuel-rich environments would be to assume a structure for these molecules, estimate thermochemical data, and calculate their relative importance under the fuel-rich conditions of interest. The $\text{Si}_2(\text{OH})_6$ molecule could take on several structures. One possible structure is an ethane-like molecule. This molecule is not likely to form because of the instability of the Si-Si bond as was confirmed by Chemkin calculations [13]. Another possible molecular structure would be analogous to Al_2I_6 and would involve some kind of OH bridging bonds [14]. A molecule such as $\text{Si}_2\text{O}_5\text{H}_6$, while not following the pressure dependence as well as $\text{Si}_2(\text{OH})_6$, has a more satisfying structure in that a Si-O-Si backbone with one H and two OH groups bonded to each Si can be envisioned [13]. Additional thermochemical property estimation is required to determine if either of the last two structures explains the observed results.

CONCLUSIONS

SiO_2 has been found to form a variety of volatile Si-O-H species in water-vapor containing environments depending on pressure, temperature and gas chemistry. Volatile Si-O-H species which are large molecules tend to form at higher pressures and have a higher pressure dependence and a lower temperature dependence. The species $\text{Si}_2\text{O}_5\text{H}_6$ or $\text{Si}_2(\text{OH})_6$ may explain the SiO_2 volatility observed in high pressure fuel-rich combustion conditions.

REFERENCES

- [1] N.S. Jacobson, J. Am. Ceram. Soc., 76 [1] 3-28 (1993).
- [2] E.J. Opila and R.E. Hann, J. Am. Ceram. Soc., 80 [1] 197-205 (1997).

- [3] R.C. Robinson and J.S. Smialek, "SiC Recession due to SiO₂ Scale Volatility under Combustor Conditions. Part I: Experimental Results and Empirical Model," submitted to J. Am. Ceram. Soc.
- [4] D.L. Hildenbrand and K.H. Lau, J. Chem. Phys. 101 [7] 6076-9 (1994). And D.L. Hildenbrand and K.H. Lau, "Revision of Thermochemical Data for SiO(OH)(g)," submitted to J. Chem. Phys.
- [5] M.D. Allendorf, C.F. Melius, P. Ho, and M.R. Zachariah, J. Phys. Chem. 99, 15285-15293 (1995).
- [6] O.H. Krikorian, "Thermodynamics of the Silica-Steam System," in Symposium on Engineering with Nuclear Explosives, January 14-16, 1970, Las Vegas, NV, vol. 1, p. 481, (1970), unpublished.
- [7] C.L. Darling and H.B. Schlegel, J. Phys. Chem. 97, 8207-8211 (1993).
- [8] A. Hashimoto, Geochim. Cosmochim. Acta 56, 511-32 (1992).
- [9] E.J. Opila, D.S. Fox, and N.S. Jacobson, J. Am. Ceram. Soc. 80 [4] 1009-1012 (1997).
- [10] D.S. Fox, E.J. Opila, and R.E. Hann, "Paralinear Oxidation of CVD SiC in Simulated Fuel-Rich Combustion", in preparation for J. Am. Ceram. Soc.
- [11] E.J. Opila, J.L. Smialek, R.C. Robinson, D.S. Fox, and N.S. Jacobson, "SiC Recession Due to SiO₂ Scale Volatility Under Combustion Conditions. Part II: Thermodynamics and Gaseous Diffusion Model," submitted to J. Am. Ceram. Soc.
- [12] A.W. Searcy, in Chemical and Mechanical Behavior of Inorganic Materials, A.W. Searcy, D.V. Ragone, and U. Colombo, Editors, pp. 15-32 Wiley-Interscience, NY, 1970.
- [13] private communication, M. Allendorf
- [14] private communication, D. Hildenbrand

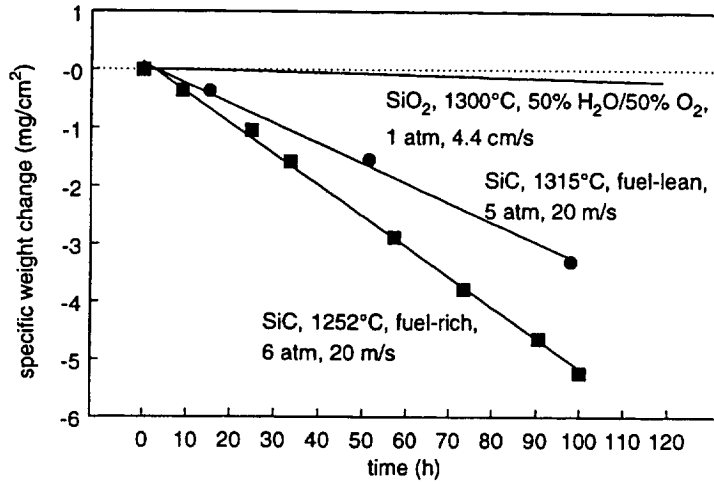


Figure 1. Silica volatility in different water-vapor or combustion environments.

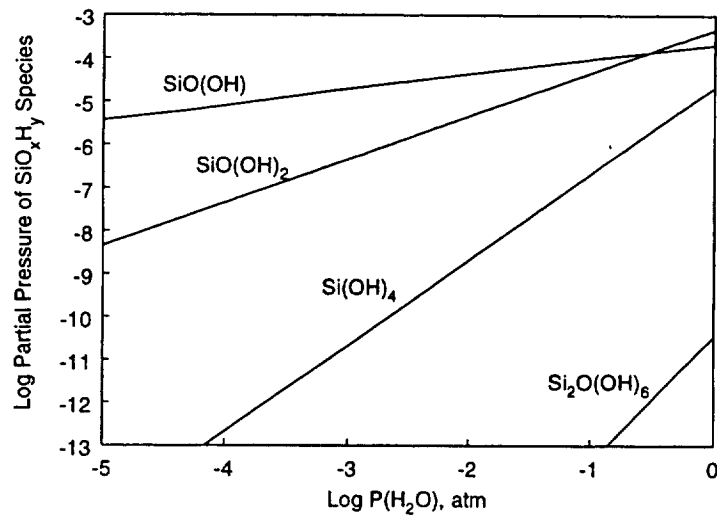


Figure 2. Si-O-H vapor species over SiO₂ at 2000K as a function of P(H₂O).

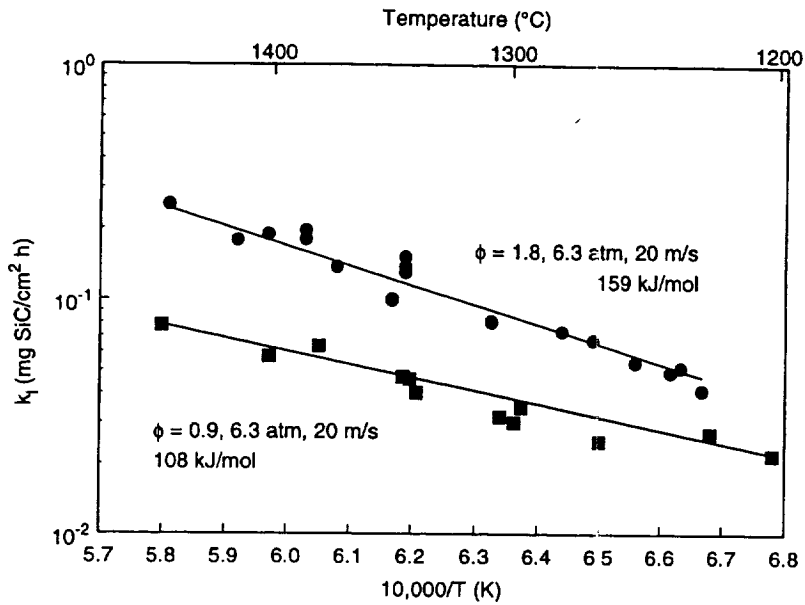


Figure 3. A comparison of silica volatility in fuel-rich ($\phi=1.8$) and fuel-lean ($\phi=0.9$) high-pressure combustion environments where ϕ is the equivalence ratio.

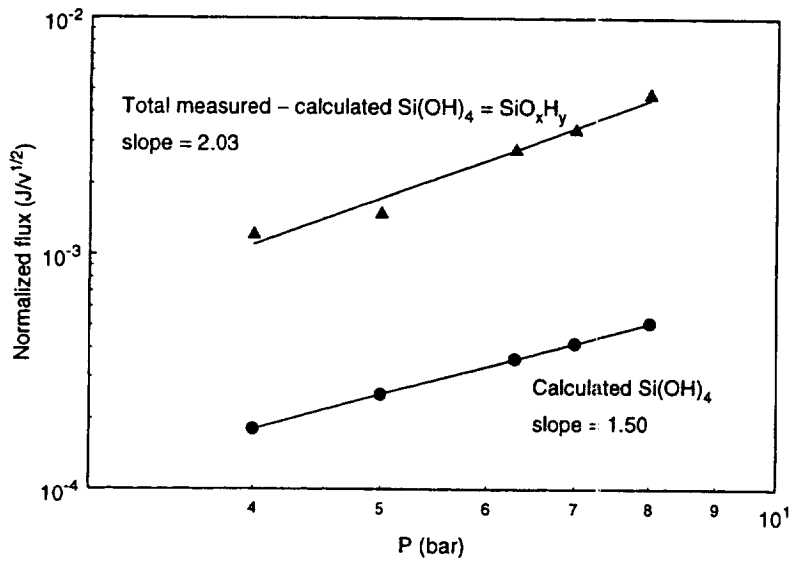


Figure 4. The pressure dependence of SiO_2 volatility in a high-pressure fuel-rich environment.

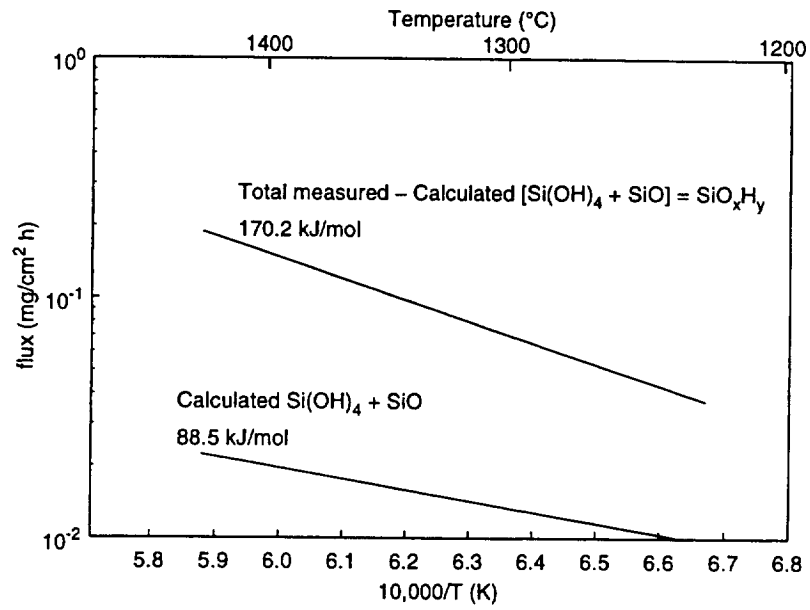


Figure 5. The temperature dependence of SiO₂ volatility in a high-pressure fuel-rich environment.

