Thermodynamics of Si(OH)\textsubscript{4} in the vapor phase of water: Henry’s and vapor–liquid distribution constants, fugacity and cross virial coefficients

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Abstract

The fugacity coefficients of Si(OH)\textsubscript{4} are evaluated from solubilities of solid phases of SiO\textsubscript{2} in the vapor phase of water. The virial equation of state, truncated at the third virial coefficient, is employed to describe the fugacity coefficients of Si(OH)\textsubscript{4}. The temperature dependencies of the second, $B_{12}$, and the third, $C_{112}$, cross virial coefficients for H\textsubscript{2}O–Si(OH)\textsubscript{4} interactions are approximated by empirical relations. It is found that silica–water interactions in the vapor phase are significantly more non-ideal compared to water–water interactions. Knowledge of $B_{12}$ and $C_{112}$ allows calculation of solubilities of quartz (Q) and amorphous silica (AS) in steam up to the density of 200 kg m\textsuperscript{-3} in satisfactory agreement with available data, and should provide reasonable solubility values at temperatures where no experimental results exist. The calculated values of the solubility of Q and AS in saturated vapor up to the critical temperature of water, $T_c$, are tabulated.

1. INTRODUCTION

There is strong and growing evidence in geochemistry that the vapor phase is an important agent for the transport of metals and metalloids under hydrothermal conditions (Williams-Jones et al., 2002; Pokrovski et al., 2005, 2008; Williams-Jones and Heinrich, 2005; Rempel et al., 2006; and many others). Modeling the vapor-phase equilibria requires knowledge of both the standard-state (an ideal gas) thermodynamic properties of formed species and their fugacity coefficients, accounting for deviations from the ideal mixing between water and other components of the vapor phase. The multicomponent nature of low-density hydrothermal solutions, the common presence of compounds of greatly varying chemical properties (neutral complex species, associated electrolytes, gases from nonpolar to strongly polar) makes the sound thermodynamic modeling of such mixtures a challenging task. However, many binary steam systems can be rigorously described employing the well-developed thermodynamic approaches for the gas mixtures and the dilute near-critical solutions.

This study presents the thermodynamic analysis of the SiO\textsubscript{2}–H\textsubscript{2}O system in the vapor phase up to the water density of 200 kg m\textsuperscript{-3}, including the near-critical ranges. The applications may include modeling of the vapor transport
of silica in the Earth crust. Additionally, there are technological uses of the results of this work. It is known that the solubility of silica in steam, although generally low, can cause significant issues for the geothermal energy production as the amount of silica transported in steam is in the range of tens to hundreds kg year\(^{-1}\) for a geothermal plant of a medium size (James, 1986). Even for non-geothermal power plants, despite a careful and expensive water treatment, the deposition of silica from the vapor phase in steam turbines is a long-standing problem (Straub and Grabowski, 1945; Heitmann, 1964; Martynova et al., 1972, 1975; Harvey and Bellows, 1997) as silica deposits restrict the steam flow, resulting in loss of the turbine power output, and may even cause structural damage. In many works the solubility of silica in the vapor phase was described by empirical equations correlating the solubility with the water density (Martynova, 1964; Fournier and Potter, 1982; Manning, 1994; Harvey and Bellows, 1997, and others) over restricted temperature and density intervals. Here a thermodynamic analysis of the problem in terms of fugacity coefficients of silica relative to the ideal gas state is presented.

The dissolution of solid phases of silicon dioxide in steam occurs mainly according to the following reaction:

\[
\text{SiO}_2(s) + 2\text{H}_2\text{O}(g) = \text{Si(OH)}_4(g).
\]

It is known (Opila et al., 1999) that at water pressures below 0.1 MPa the contribution of \(\text{Si(OH)}_2\) to the material balance of silica is 10–30 times less than that of \(\text{Si(OH)}_4\). As the concentration of \(\text{Si(OH)}_2\) increases in equilibrium with \(\text{SiO}_2(s)\) raises linearly with water pressure, whereas the concentration of \(\text{Si(OH)}_4\) raises proportionally to the square of water pressure, at higher steam pressures the contribution of \(\text{Si(OH)}_2\) is expected to become negligible. It must be mentioned that the aqueous chemistry of silica is strongly complicated by polymerization and interaction with other solutes (Zotov and Keppler, 2000, 2002; Newton and Manning, 2003; Gerya et al., 2005; Newton and Manning, 2008a,b; Hunt et al., 2011). However, the data treatment in the current work was carried out in terms of a single species \(\text{Si(OH)}_4\), since the effects of polymerization depend strongly on the total silica concentrations and are expected to be minute at T-P-x conditions under consideration. Preliminary estimates of the contribution of a dimer to the material balance of silica in steam can be made as follows. Tossell (2005) performed quantum mechanical calculations of the energetics of the dimerization of monosilicic acid according to the reaction

\[
2\text{Si(OH)}_2(g) = \text{Si}_2\text{O}_7\text{H}_6(g) + \text{H}_2\text{O}(g).
\]

In this work, dedicated to the determination of the thermodynamic properties of \(\text{Si(OH)}_4\) in the vapor phase of water, the ideal-gas standard-state convention is chosen for \(\text{Si(OH)}_4\) and water as defined by IUPAC (Mills et al., 1993): “the standard state for a gaseous substance, whether pure or in a gaseous mixture, is the (hypothetical) state of the pure substance in the gaseous state at the standard pressure \(P = P^\circ\) and exhibiting ideal gas behaviour.” The standard state for solid phases of the \(\text{SiO}_2\) composition “is the state of the pure substance… in the solid state at the standard pressure \(P = P^\circ\)” (Mills et al., 1993).

For calculations of Henry’s constants (Section 3), the standard state of the solute \(\text{Si(OH)}_4\) in the liquid phase of water “is the state… at the standard molality…” \(m = 1\), at a given pressure \(P\), “exhibiting infinitely diluted solution behaviour” (Mills et al., 1993).

The standard pressure \(P^\circ\) is taken equal to 0.1 MPa. In the binary mixture \(\text{H}_2\text{O}-\text{Si(OH)}_4\) water is designated as component 1, and \(\text{Si(OH)}_4\) as component 2. The word “steam” is used as the synonym of the “vapor phase of water”. The values of properties of water are calculated using the equation of state of Wagner and Prüß (2002).

For equilibrium thermodynamic calculations involving \(\text{Si(OH)}_4\) in a gaseous mixture it is necessary to calculate the chemical potential of this species, \(\mu_2\), according to the expression:

\[
\mu_2(T, P) = \mu_2^\circ(T) + RT \ln f_2 = \mu_2^\circ(T) + RT \ln P_2\varphi_2,
\]

where \(T\) and \(P\) designate temperature and pressure, respectively; \(y_2\) is the mole fraction of \(\text{Si(OH)}_4\) in a gas mixture; \(\mu_2^\circ(T)\) is the chemical potential in the ideal gas state; \(f_2\) and \(\varphi_2\) stand for the fugacity and the fugacity coefficient of \(\text{Si(OH)}_4\), respectively. Fugacity coefficients of many solutions may be evaluated from the cubic equations of state (Prausnitz et al., 1999), but not for \(\text{Si(OH)}_4\) due to lack of necessary data on the critical properties and vapor pressures. However, the virial equation of state may be used for...
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