

Evaluation of thermodynamic properties of H_4SiO_4 in the ideal gas state from experimental data

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Thermodynamic properties of gaseous silicon hydroxides are necessary for analyzing the silicate condensation phenomena in the primordial solar nebula [Hashimoto, 1992], the silica precipitation in steam-rich geothermal systems and recent concerns with the corrosion or deposition of SiO_2 -containing alloys and ceramics in high-temperature moist environments.

Experimental transpiration studies (i.e. studies of the partial pressures of Si over solid phases in the presence of steam) of the reaction of water vapor with cristobalite [Hashimoto, 1992; Jacobson, et al., 2005] agree that at 1100–1650 K and water pressures close to 0.1 MPa the vapor phase concentration of Si is determined by the reaction



Mass spectrometric data on the volatile species formed from $SiO_2(s)$ and water at 1473–1773 K and water vapor pressure between 0.018 and 0.094 MPa [Opila, et al., 1997] also confirm that H_4SiO_4 is the primary reaction product. However, the literature data on the thermodynamic properties of gaseous H_4SiO_4 [Allendorf, et al., 1995; Jacobson, et al., 2005; Rutz and Bockhorn, 2005] differ up to $18 \text{ kJ}\cdot\text{mol}^{-1}$ and $9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in the value of enthalpy of formation and the entropy at $T_r=298.15 \text{ K}$ and the standard pressure $P^\ominus = 0.1 \text{ MPa}$.

Therefore, it was decided employ all available data for the reaction (1) to determine the optimal values of $\Delta_f G^\ominus$ and S^\ominus of $H_4SiO_4(g)$ at 298.15 K and 0.1 MPa.

Selection of experimental data

In addition to the transpiration data we accepted data on the solubility of quartz and amorphous silica in water vapor of density below $15 \text{ kg}\cdot\text{m}^{-3}$. The accepted data set of data to calculate the values of equilibrium constant of reaction (1) is given in Table.

Table. Data sets used in the determination of $\Delta_f G^\ominus$ and S^\ominus of $H_4SiO_4(g)$ at 298.15 K and 0.1 MPa

Reference	Solid Phase ^a	T range, K	P range, MPa	Number of points	$ \overline{\Delta} ^b$ J·mol ⁻¹
[Straub and Grabowski, 1945]	AS	533.2–616.5	0.345–2.76	32	579
[Morey and Hesselgesser, 1951]	Q	673.2–773.2	3.45–6.89	3	4322
[Wendlandt and Glemser, 1963] ^c	Q	673.2	2.128	1	3497
[Heitmann, 1964] ^d	AS	572.2–776.2	0.88–4.90	21	871
[Heitmann, 1964] ^d	Q	624.2–865.2	0.88–4.90	6	907
[Martynova, et al., 1975]	AS	424.25–496.06	0.49–2.45	3	417
[Hashimoto, 1992] ^c	CR	1375–1661	≤0.1	10	182
[Jacobson et al., 2005]	CR	1074–1375	≤0.1	26	946

^aAS, Q, CR designates amorphous silica, quartz, cristobalite, respectively

^b $|\overline{\Delta}|$ is the average of the absolute values of the difference between experimental and calculated

$G_{T,P^\ominus}^\ominus(H_4SiO_4(g))$.

^cThe numerical values are quoted from the review of [Harvey and Bellows, 1997].

^dWeight of data points is taken equal to 0.5.

*Primary data are not reported in the paper, however, most data points are tabulated in [Jacobson, et al. 2005].

Based on critique of Heitsmann' data by [Martynova, et al., 1975] and [Harvey and Bellows, 1997], only data at T>550 K and P>0.6 MPa from [Heitmann, 1964] were included in the set. At 773 K results of [Morey and Hesselgesser, 1951] and [Heitmann, 1964] of quartz solubility are comparable, however, values of [Wendlandt and Glemser, 1963] are up to 3–4 times lower, therefore, the latter data at this temperature were excluded.

Data treatment

The expression for $\ln K^o$ of the reaction (1) with a good approximation is given by

$$\ln K^o = \ln \frac{Y \cdot \phi_{H_4SiO_4}^\infty \cdot P^\ominus}{P \cdot (\phi_{H_2O}^*)^2} - \frac{V(SiO_2(s)) \cdot (P - P^\ominus)}{RT} \quad (2)$$

where Y stands for the mole fraction of silica in the vapor phase, $\phi_{H_2O}^*$ is the fugacity coefficient of water, $\phi_{H_4SiO_4}^\infty$ is the partial molar fugacity coefficient of dissolved silica at infinite dilution in water, V stands for the molar volume of solid silicon dioxide phase. The values of the fugacity coefficient of water, $\phi_{H_2O}^*$, are accurately known over very wide T and P ranges [Wagner and Pruyß, 2002], however, $\phi_{H_4SiO_4}^\infty$ is not known.

2 models for the fugacity coefficients were used in our data treatment:

1). An ideal mixture of ideal gases, i.e. $\phi_{H_2O}^* = 1$ and $\phi_{H_4SiO_4}^\infty = 1$.

2). An approximation, based on preliminary results for boric acid and H₄SiO₄ that $B_{12}(T) \approx n \cdot B_{11}(T)$, where n is close (within ± 1) to the number of OH groups in the molecule of a hydroxide, i.e. $B_{12}(T) = 4 \cdot B_{11}(T)$ for the interactions between molecules of H₂O and H₄SiO₄. Here B_{11} is the well-known second virial coefficient of water [Harvey and Lemmon, 2004], B_{12} is the second cross virial coefficient for interactions between molecules H₂O and H₄SiO₄. According to thermodynamic textbooks [Prausnitz, et al., 1999]: $\ln \phi_{H_2O}^* = \frac{B_{11}(T) \cdot P}{RT}$ and

$\ln \phi_{H_4SiO_4}^\infty = (2B_{12}(T) - B_{11}(T)) \frac{P}{RT}$. This model is considered to be more realistic compared to the model of ideal mixing of ideal gases.

Calculated values of $\ln K^o$ were converted to the Gibbs energy change, $\Delta_r G^o(T)$, for the reaction (1) at the ideal gas standard state pressure of 0.1 MPa according to:

$$\Delta_r G^o(T) = -RT \ln K^o = G_T^o(H_4SiO_4(g)) - 2G_T^o(H_2O(g)) - G_T^o(SiO_2(s)). \quad (3)$$

The value of $\Delta_r G^o(T)$ is the stoichiometric sum of the Gibbs energies, G_T^o , of the reaction (1) participants at the standard state pressure of 0.1 MPa, which are given by

$$G_T^o = \Delta_f G_{T_r}^o - S_{T_r}^o(T - T_r) + \int_{T_r}^T C_p^o dT - T \int_{T_r}^T \frac{C_p^o}{T} dT. \quad (4)$$

Then, for each experimental point the values of the auxiliary function F were calculated as follows:

$$F = \Delta_r G^o + 2G_T^o(H_2O(g)) + G_T^o(SiO_2(s)) - \int_{T_r}^T C_p^o(H_4SiO_4(g)) dT + T \int_{T_r}^T \frac{C_p^o(H_4SiO_4(g))}{T} dT. \quad (5)$$

It follows that

$$F = \Delta_f G_{T_r}^o(H_4SiO_4(g)) - S_{T_r}^o(H_4SiO_4(g)) \cdot (T - T_r). \quad (6)$$

In total, 102 values of F over the temperature range 424-1661 K were collected. The weighted least-squares fit of all data resulted in the following values at 298.15 K for H₄SiO₄(g) :

1). An "ideal mixture of ideal gases" model: $\Delta_f G^o = -1239.74 \pm 0.53$ kJ·mol⁻¹; $S^o = 346.65 \pm 0.75$ J·K⁻¹·mol⁻¹.

2). An approximation $B_{12} = 4 \cdot B_{11}$: $\Delta_f G^o = -1238.51 \pm 0.51$ kJ·mol⁻¹; $S^o = 347.78 \pm 0.72$ J·K⁻¹·mol⁻¹, with uncertainties given as 2σ . This result is considered more realistic.

Taking into account the effect of uncertainty of thermodynamic functions of solid phases and, what is most important, the uncertainty in the heat capacity of H₄SiO₄(g) (data of [Allendorf, *et al.* 1995; Rutz and Bockhorn, 2005] differ from 2 to 8%), the final recommendations of the thermodynamic properties of H₄SiO₄ are as follows: $\Delta_f G^\circ = -1238.51 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$; $S^\circ = 347.78 \pm 6.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $\Delta_f H^\circ = -1340.68 \pm 3.5 \text{ kJ}\cdot\text{mol}^{-1}$, with necessary values of S° for H₂(g), O₂(g), Si(c) taken from [Cox, *et al.*, 1989]. The heat capacity of H₄SiO₄(g) at 250–2000 K from data of [Allendorf, *et al.*, 1995] was approximated by a polynomial: $C_p^\circ/R = a_0 + a_1 \cdot 10^{-2} \cdot T + a_2 \cdot 10^{-5} \cdot T^2 + a_3 \cdot 10^{-8} \cdot T^3 + a_4 \cdot 10^{-11} \cdot T^4 + a_5 \cdot 10^{-15} \cdot T^5$, where $a_0 = 2.87914$; $a_1 = 5.89126$; $a_2 = -9.47715$; $a_3 = 7.84564$; $a_4 = -3.15382$; $a_5 = 4.89073$.

For graphical presentation all data were recalculated to the Gibbs energy change, $\Delta_{sol} G^\circ$, of the reaction SiO₂(quartz) + 2H₂O(g) = H₄SiO₄(g), see Figure, which shows the values of $\Delta_{sol} G^\circ$ calculated from various data sets (symbols). The solid line is calculated using the values of the thermodynamic functions of H₄SiO₄(g) obtained in this study, while the dashed line corresponds to the thermodynamic functions of H₄SiO₄(g) from [Jacobson, *et al.*, 2005].

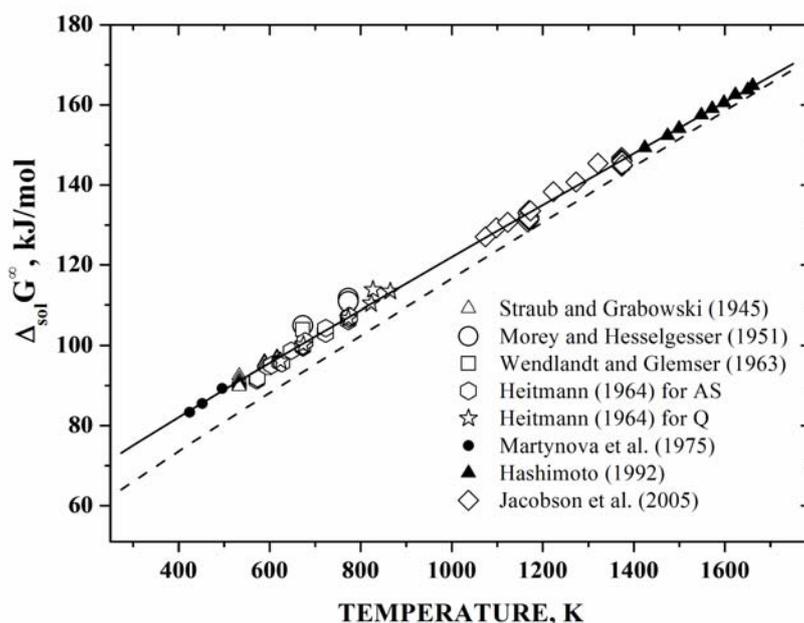


Fig. Values of $\Delta_{sol} G^\circ$ at $P^\circ = 0.1 \text{ MPa}$ for the reaction $\text{SiO}_2(\text{quartz}) + 2\text{H}_2\text{O}(\text{g}) = \text{H}_4\text{SiO}_4(\text{g})$, calculated using values of the auxiliary function F from various sets of data (symbols), or using the thermodynamic functions of H₄SiO₄(g) recommended in this work (solid line) or by [Jacobson, *et al.*, 2005] (dashed line).

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