Thermodynamic Model for SnO_2(cr) and SnO_2(am) Solubility in the Aqueous Na^+–H^+–OH^-–Cl^-–H_2O System

Dhanpat Rai · Mikazu Yui · H. Todd Schaef · Akira Kitamura

Abstract The solubility of SnO_2(cassiterite) was studied at $23 \pm 2\,°C$ as a function of time (7 to 49 days) and pH (0 to 14.5). Steady state concentrations were reached in <7 days. The data were interpreted using the SIT model. The data show that SnO_2(cassiterite) is the stable phase at pH values of $< \sim 11.7$. These extensive data provided a $\log_{10} K^0$ value of -64.39 ± 0.30 for the reaction (SnO_2(cassiterite) $+2H_2O \rightleftarrows Sn^{4+} + 4OH^-$) and values of 1.86 ± 0.30, ≤ -0.62, -9.20 ± 0.34, and -20.28 ± 0.34 for the reaction ($Sn^{4+} + nH_2O \rightleftarrows Sn(OH)_n^{4-n} + nH^+$) with values of "$n$" equal to 1, 4, 5, and 6 respectively. These thermodynamic hydrolysis constants were used to reinterpret the extensive literature data for SnO_2(am) solubility, which provided a $\log_{10} K^0$ value of -61.80 ± 0.29 for the reaction (SnO_2(am) $+ 2H_2O \rightleftarrows Sn^{4+} + 4OH^-$). SnO_2(cassiterite) is unstable under highly alkaline conditions (NaOH concentrations >0.003 mol·dm^{-3}) and transforms to a double salt of SnO_2 and NaOH. Although additional well-focused studies will be required for confirmation, the experimental data in the highly alkaline region (0.003 to 3.5 mol·dm^{-3} NaOH) can be well described with $\log_{10} K^0$ of -5.29 ± 0.35 for the reaction $Na_2Sn(OH)_6$(s) $\rightleftarrows Na_2Sn(OH)_6$(aq).

1 Introduction

^{126}Sn, one of the seven long-lived fission products, has a half life of about 10^5 years [1]. Therefore, it is an important element in the management of high-level radioactive wastes.

D. Rai (✉)
Rai Enviro-Chem, LLC, 1000 Hanley Drive, P.O. Box 784, Yachats, OR 97498-0784, USA
e-mail: dhan.rai@raienvirochem.com

M. Yui · A. Kitamura
Japan Atomic Agency, Tokai-mura, Japan

H.T. Schaef
Pacific Northwest National Laboratory, Richland, WA, USA

Among the several different oxidation states of tin, only the +II and +IV are important in aqueous chemistry. The tin + II state exists only in very reducing conditions, so the +IV state is the most important under most geologic conditions [2]. Reliable values of thermodynamic constants, especially pertaining to the solubility of Sn(IV) compounds and hydrolysis constants of Sn(IV), are required to predict the behavior of tin contained in radioactive wastes disposed in geologic environments.

The thermodynamic data for tin have been reviewed by several authors and somewhat more recently by Lothenbach et al. [3] and Seby et al. [4]. No new data for the Sn(IV)–hydroxide system have become available since these reviews. Seby et al. [4] noted disparate results for the hydrolysis complexes and species and concluded that SnO_3^{2-} (or its alternate designation, $Sn(OH)_6^{2-}$) is expected to be important in alkaline conditions but did not recommend values for any of the hydrolysis constants or the solubility product of cassiterite. Lothenbach et al. [3], on the other hand, based on a study by Amaya et al. [2],[1] which was not reviewed by Seby et al. [4], selected values for the formation of $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ from $Sn(OH)_4(aq)$. The thermodynamic data for Sn(IV) hydrolyses are (1) relatively old, from a time when some of the newer analytical and speciation techniques or data interpretation models were not available, (2) based mostly on the solubility of $SnO_2(cr)$ in a pH region where the measured concentrations are at or near the detection limit, making it difficult to obtain reliable values, (3) unavailable or unreliable for some key reactions, (4) limited in most cases in that only one value is available for a given reaction and no other confirmatory value is available and (5) conflicting in that the reported equilibrium constant values differ by several orders of magnitude. These points are further elaborated below.

Estimated $\log_{10} K^0$ values (ranging from −63.7 to −64.5) for the cassiterite solubility reaction ($SnO_2(cassiterite) + 2H_2O \rightleftharpoons Sn^{4+} + 4OH^-$) are reported in various compilations [4, 6, 7]. Several attempts have been made in the past (e.g., see [2, 8–11]) to experimentally determine the solubility product and obtain values of various Sn(IV) hydrolysis constants from the solubility of cassiterite as a function of pH at values between 2 and 8. Although there are differences in the total measured Sn(IV) concentrations (ranging from about 10^{-5} to 10^{-8} mol·dm^{-3}), the measured concentrations reported by these authors in this pH range are very low and independent of pH. All SnO_2 solids, especially cassiterite, are relatively insoluble and hydrolyze even under acidic conditions,[2] and between pH = 2 and 8 the differences in measured Sn(IV) concentrations most likely reflect the detection limits or are controlled by the presence of a small amount of colloids rather than an equilibrium with $Sn(OH)_4(aq)$ species ($SnO_2(cr) + 2H_2O \rightleftharpoons Sn(OH)_4(aq)$) as the authors propose. Even if one assumes that their proposed reaction is correct, because of detection limit concerns and the possible presence of colloids due to ineffective methods of separating solids from solutions in many cases, the only value that could be proposed for the above reaction would be an upper limit similar to that reported for other species in equilibrium with solids of different elements that show pH-independent concentrations and are sparingly soluble (e.g., see [13, 14]). Such values can be considered in calculating upper limit concentrations, but they are not accurate, certainly not accurate enough for use in calculating the values for other constants. Therefore, to obtain meaningful solubility data, the studies must also be conducted in the very acidic region (pH < 2) where the expected solubility will be high and complications due to detection limits and colloids can be avoided.

Only one study [15] was carried out under acidic conditions. In this study, the spectrophotometric method was used to obtain hydrolysis constants of Sn(IV) from acidic

---

[1] Also see Oda and Amya [5] where the same data are also included.

[2] Huey and Tartar [12] observed the predominance of Sn^{4+} in only >0.5 mol·dm^{-3} HCl solutions.

1.0 mol·dm^{-3} KNO$_3$. The values for the formation constants for the reaction (Sn^{4+} + nH$_2$O $\rightleftharpoons$ Sn(OH)$_n^{4-n}$ + nH$^+$) with "n" varying from 1 to 4 are reported. There are uncertainties in the reported values because of the possible complexation/interaction of Sn^{4+} with relatively high concentrations of nitrate used as the background electrolyte, and no other confirmatory values for these reactions are available (further details for this study are provided in the results and discussion section).

It is well documented that SnO$_2$ solids show amphoteric behavior due to the formation of anionic complexes Sn(OH)$_5^-$ and Sn(OH)$_6^{2-}$) [2, 5, 8]. Macchi and Pettine [16], using differential pulse anodic stripping voltammetry (DPASV), also reported the presence of SnO(OH)$_3^-$ (alternately Sn(OH)$_5^-$) but provided no values of the equilibrium constant for the formation of this species. Although the anionic species are documented: (1) the log$_{10}$ K^0 value of -12.4 reported for the reaction [Sn(OH)$_4$(aq) + H$_2$O $\rightleftharpoons$ Sn(OH)$_5^-$ + H$^+$] by Barsukov and Klintsova [8] differs by over four orders of magnitude compared to the value (-7.97) reported by Oda and Amaya [2], and (2) Oda and Amaya [2] report a log$_{10}$ K^0 value of -18.38 for the reaction [Sn(OH)$_4$(aq) + 2H$_2$O $\rightleftharpoons$ Sn(OH)$_6^{2-}$ + 2H$^+$], but no confirmatory value for this reaction is available. Considering that all of these values are pegged to the Sn(OH)$_4$(aq) species and the values for this species cannot be considered reliable, it casts doubt on the accuracy of the reported values. However, since Oda and Amaya [2] determined the values for the formation of both Sn(OH)$_5^-$ and Sn(OH)$_6^{2-}$ from Sn(OH)$_4$(aq), the log$_{10}$ K^0 value of -10.41 that we calculate from their data for the reaction [Sn(OH)$_5^-$ + H$_2$O $\rightleftharpoons$ Sn(OH)$_6^{2-}$ + 2H$^+$], where the Sn(OH)$_4$(aq) species cancel out, may be reasonable. Seby et al. [4] quote an estimated log$_{10}$ K^0 value of -23.47 for the reaction [Sn^{4+} + 3H$_2$O $\rightleftharpoons$ SnO$_3^{2-}$ + 6H$^+$] that they attribute to Pourbaix [17], but this value can neither be compared directly to the values quoted above nor is any other value for this reaction available for comparisons.

It is clear from the above discussion that SnO$_2$ solids are expected to show amphoteric behavior and (1) reliable thermodynamic data for the hydrolysis complexes and the solubility products of the important Sn(IV) solid phases are not available, and (2) solubility studies with well-characterized solids covering very acidic to very basic conditions will be required to obtain meaningful data. Therefore, the objectives of this study were to obtain reliable values for the solubility product of SnO$_2$(cassiterite) and hydrolysis constants. To meet these objectives, we have: (1) determined the solubility of SnO$_2$(cassiterite) in a large range of pH values ($\sim$0.03 to 14.4), and (2) reinterpreted the raw good-quality literature data, where available, to determine values for various reactions based on all available data. These efforts have resulted in reliable thermodynamic data for the solubility products of SnO$_2$(cassiterite) and SnO$_2$(am), the hydrolysis constants for the formation of SnOH^{3+}, Sn(OH)$_5^-$, Sn(OH)$_6^{2-}$, and the upper limit value for the formation of Sn(OH)$_4$(aq) from Sn^{4+}.

2 Methods and Materials

2.1 Reagents and Stock Solutions

The SnO$_2$(cr) (lot # 063082) was purchased from Alpha Chemical Products. The X-ray diffraction analyses of this solid confirmed it to be similar to synthetic crystalline cassiterite (Table 1). HCl and carbonate-free NaOH were from Anachemia Acculate.

The deionized water was in all cases deaerated by boiling and transferring the hot water to an atmospheric control chamber containing N$_2$ (>99%) maintained at 23 ± 2 °C. Required stock solutions of NaOH and HCl were prepared in an inert atmosphere, using deaerated water.

Table 1 Comparisons of d-spacings and their percent relative intensities (% RI), based on X-ray diffraction analyses of equilibrated samples compared to the solid originally used in this study

| PDF number 00-041-1445 | | Original solid | | 22 day equilibrated samples[a] | | | | | |
| | | | | 127 | | 130 | | 135 | |
d Å	% RI	d Å	% RI	d Å	% RI	d Å	% RI	d Å	% RI
								5.21	70
3.3470	100	3.34	100	3.34	100	3.34	100	3.34	100
								2.95	17
2.6427	75	2.63	85	2.63	87	2.64	76	2.63	94
								2.54	15
2.3690	21	2.35	21	2.375	23	2.36	24	2.375	39
2.3094	4	2.3	5	2.302	4	2.31	4	2.302	9
								1.88	8
1.7641	57	1.76	64	1.76	68	1.76	59	1.76	94
1.6750	14	1.67	15	1.673	14	1.67	12	1.673	24
1.5934	6	1.59	7	1.592	6	1.592	5	1.592	9

[a]The Sample 127 pH = 9.59. Samples 130 and 135 were equilibrated with 0.01 and 3.5 mol·dm^{-3} NaOH, respectively

2.2 General Procedure

Two sets of experiments, one in the acidic region (pH < 3.4) and the other covering a wide range in pH values (6 to 14.4) obtained by adding various amounts of HCl or NaOH, were conducted. Both sets of experiments used Oak-Ridge type 50 mL glass-centrifuge tubes that were washed with acid and thoroughly rinsed with deionized water. All experiments were conducted at 23 ± 2 °C. In the Set I experiments approximately 50 mg portions of $SnO_2(cr)$ in centrifuge tubes were suspended in 40 mL of HCl solutions of varying molalities, ranging between 1.0 and 0.0003 mol·dm^{-3}, to obtain a range in pH values between 0.0 and 3.5 (see Appendix Table 6 for details).

In the Set II experiments, 50 mg of $SnO_2(cr)$ were suspended in 40 mL of deionized water adjusted to different pH values using standard HCl or NaOH solutions to obtain a range in pH values between 6 and 14.4 (see Appendix Table 7 for details).

The centrifuge tubes containing $SnO_2(c)$ suspensions in various solutions were sealed and then gently agitated continuously by placing them on a shaker until they were analyzed. The Set I samples were agitated on the bench top and Set II samples were agitated in an atmospheric control chamber filled with purified $N_2(g)$ (>99%) containing <10 ppm $O_2(g)$. At different equilibration periods, the pH of the suspensions was measured with a combination glass electrode (Ross-Orion) that was calibrated against certified pH buffers ranging in values from 0.5 to 12.

At the end of the various equilibration periods, suspensions were centrifuged at about 2000 g for 20 minutes. Aliquots of supernatants were withdrawn and filtered through Amicon Centricon-30 (Amicon Corp., Lexington, Massachusetts) with effective 30,000 molecular-weight cutoffs and approximate 0.004 μm pore sizes. To increase the efficacy of the filters for separating solids from solutions, the filters were pretreated as described by Rai [18] following these steps: (1) the filters were washed and equilibrated with deionized water adjusted to the pH of the samples to prevent changes in Sn concentration during filtration due to possible changes in pH; and (2) a 1 mL aliquot of the sample was first passed

through the filter to saturate any possible adsorption sites on the filters and filtration containers (this filtrate was discarded). Samples in Set II containing relatively high concentrations of NaOH (reaching as high as 3.5 mol·dm^{-3}) at a 15 day equilibration period were either unfiltered (centrifuged only) or filtered using a syringe system, which does not allow filter membranes to be separated from the backing that can occur at high concentrations of NaOH, to test whether the results with the filters can be relied upon for the suspensions that contain relatively concentrated NaOH. All filtrates were acidified with HCl and analyzed for Sn with inductively coupled plasma mass spectroscopy (ICP-MS) or by inductively coupled plasma optical emission spectroscopy (ICP-OES). See Appendix Tables 6 and 7 for a complete listing of experimental data.

The original $SnO_2(cr)$ solid and selected solids from equilibrated samples from Set II were analyzed by X-ray diffraction using CuKα radiation.

2.3 Thermodynamic Modeling

The solubility data were interpreted using the SIT model as implemented in the coupled nonlinear least squares and chemical equilibrium program, NONLINT-SIT, based on minimization of the Gibbs energy. A general description of this code is given in Rand et al. [14]. The NONLINT-SIT (personal communication, 2004, A.R. Felmy, Pacific Northwest National Laboratory, WA, USA) is an extended version of the GMIN, NONLIN and NONLINT codes described in Felmy [19] and Sterner et al. [20]. In this program the actual quantity minimized is the standard deviation, defined as Eq. 1 where N is the total number of data points

$$\sigma = \sum_{i=1}^{N} [\{f(x)\}^2/N]^{1/2} \tag{1}$$

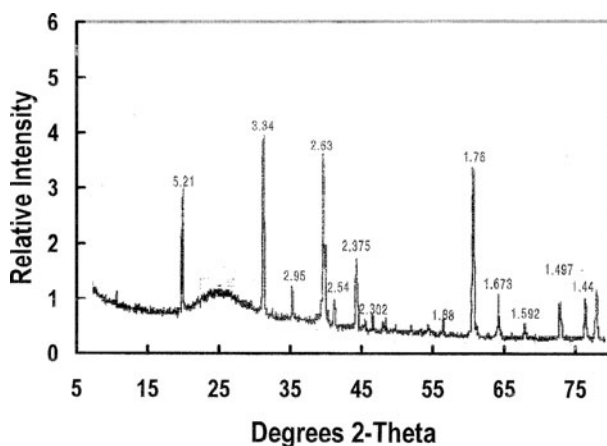and $f(x)$ is given by the phase equilibrium Eq. 2 wherein ΔG_{solid} is the iteratively-fitted

$$f(x) = \Delta G_{\text{solid}} - \Delta G_{\text{solution}} \tag{2}$$

dimensionless Gibbs energy ($\Delta_f G_m^\circ/RT$) of the solid phase and $\Delta G_{\text{solution}}$ is the dimensionless Gibbs energy calculated from the experimental aqueous phase data and the associated ion-interaction model parameters (or equivalently the chemical potential of the second phase). In the simplest case of $SnO_2(cr)$ solubility, for example, [$SnO_2(cr) + 3H^+ \rightleftarrows SnOH^{3+} + H_2O$], in which $SnOH^{3+}$ is the dominant species, Eq. 2 yields Eq. 3 where $\Delta_f G_m^\circ/RT$ is the dimensionless standard molar Gibbs energies of formation for the depicted species, the quantities in square brackets are concentrations, and γ_i refers to the activity coefficient of the species i.

$$f(x) = (\Delta_f G_m^\circ/RT)_{SnO_2(cr)} - [(\Delta_f G_m^\circ/RT)_{SnOH^{3+}} + (\Delta_f G_m^\circ/RT)_{H_2O}$$
$$+ \ln[SnOH^{3+}]\gamma_{SnOH^{3+}} - 3\ln[H^+]\gamma_{H^+}] \tag{3}$$

All of the variables in Eq. 2 except [$((\Delta_f G_m^\circ/RT)_{SnOH^{3+}}$] are either known or calculated. The activity coefficients (γ_i) were calculated from SIT ion-interaction parameters.

3 Results and Discussion

3.1 SnO$_2$(cr) Solubility Data

Crystalline SnO$_2$, cassiterite, is the original solid used in this study. Comparisons of the X-ray diffraction data for the original solid and the solids equilibrated at pH values of 9.59 and 12.0 show the presence of cassiterite (Table 1). Since cassiterite is the only phase present at pH = 9.59 (changes in solid phase will occur, if at all, at high pH), it can be stated that cassiterite is also the solubility-controlling solid at pH values <9.59. X-ray diffraction analyses of the sample equilibrated in 3.5 mol·dm^{-3} NaOH showed, in addition to peaks for cassiterite, additional peaks at $d/$Å of 5.21, 2.85, 2.54, and 1.88 along with a few other minor peaks (Table 1, Fig. 1). The International Center for Diffraction Data (ICDD) [21] reports a number of crystalline Na–Sn–hydroxide/oxide solid phases (Na$_2$SnO$_3$(cr), PDF#00-030-1252; Na$_2$Sn(OH)$_6$(cr), PDF#00-024-1143; Na$_2$Sn$_2$O$_5$(cr), PDF#00-021-1165; Na$_4$SnO$_4$(cr), PDF#00-032-1175 and PDF#00-027-1420) with a multitude of peaks for these solids which are expected to form under alkaline conditions such as those used in this study. We are unable to assign the pattern for our sample to any specific compound because of the lack of an exact match with any of the reported patterns, although several of the major peaks are similar to the ones reported for several of these solids. Although we are unable to definitively identify the solid phase based on these XRD analyses alone, thermodynamic analyses of the solubility data at pH values > ~11.7, discussed in detail below, are consistent with the formation of Na$_2$Sn(OH)$_6$(cr) or Na$_2$SnO$_3$(cr).

The solubility data (Fig. 2) shows that as the pH values increase the Sn(IV) concentrations in solutions in equilibrium with cassiterite decrease dramatically in the low pH region (< ~1.3) and increase at pH values > ~8. The Sn concentrations are nearly constant in the intermediate pH region (~1.3 to 8) and at pH values > ~11.7. Because of possible changes in the solid phase at high pH values (as noted above and discussed in detail later), the solubility data at pH values < ~11.7 is best suited to determining equilibrium constants for solubility reactions involving cassiterite and various hydrolysis species of Sn(IV).

Sn(IV) concentrations at any given pH are similar to each other at different equilibration periods (7, 15, 36, 38, and 49 days) (Fig. 2), indicating that steady state concentrations in this system are reached rather rapidly (<7 days). To show that equilibrium is reached in a given system, ideally it is best to approach the equilibrium from both the oversaturation and undersaturation directions. In a preliminary study, a 0.056 mol·dm^{-3} SnCl$_4$ solution adjusted
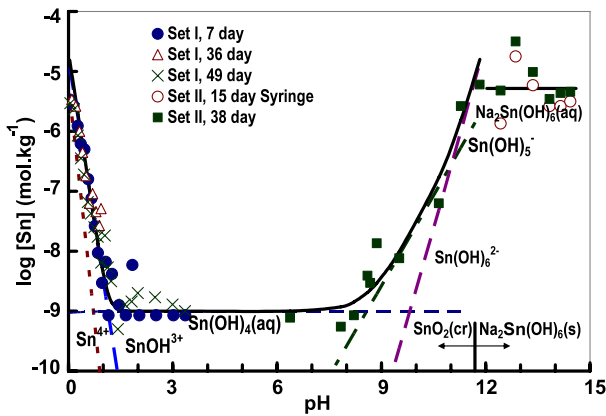
Fig. 2 Sn concentrations in filtrates (0.004 μm) from suspensions equilibrated with cassiterite (SnO_2) at pH values of $\leq \sim 11.7$, and with $Na_2Sn(OH)_6(s)$ at pH values $> \sim 11.7$, for different time periods as a function of pH. The pH values of samples at pH $>$ 12 were estimated from hydroxide activities (a_{OH}) (pH $= 14 + \log_{10} a_{OH}$) determined using the SIT model (NONLINT-SIT); for an accurate plot of these data as a function of hydroxide concentration see Fig. 6. The *thick solid line* depicts total predicted Sn concentrations in equilibrium with cassiterite based on NONLINT-SIT calculations using the SIT based thermodynamic model (Tables 2 and 4); the other lines represent predicted concentrations of different species as identified

Table 2 Values of SIT ion-interaction parameters for different species used in this study

| Species	ε (kg·mol^{-1})	Reference
H^+, Cl^-	0.12 ± 0.01	[14]
H^+, ClO_4^-	0.14 ± 0.02	[14]
Na^+, OH^-	0.04 ± 0.01	[14]
Na^+, Cl^-	0.03 ± 0.01	[14]
Na^+, ClO_4^-	0.01 ± 0.01	[14]
Na^+, OH^-	0.04 ± 0.01	[14]
Sn^{4+}, Cl^-	0.25 ± 0.03	This study[a]
Sn^{4+}, ClO_4^-	0.78	This study[b]
$SnOH^{3+}$, Cl^-	0.19 ± 0.05	This study[a]
Na^+, $Sn(OH)_5^-$	-0.08	This study[c]
Na^+, $Sn(OH)_6^{2-}$	-0.125	This study[c]

[a] Assuming that the ion interaction parameters for the analogous thorium species (Th^{4+}, Cl^-; $ThOH^{3+}$, Cl^-) are identical to those for the tin species listed here

[b] An average of ε values reported for other tetravalent ions reported in Rand et al. [14]

[c] Representative ε values for other species of other singly or doubly negatively charged species with Na^+ reported in Rand et al. [14]

initially to pH $= 1.184$, after 14 days of equilibration showed a lower pH value (0.76) and $\log_{10}[Sn] = -5.53$ along with precipitation of a Sn(IV) solid. The decrease in pH is consistent with the precipitation of a SnO_2 solid. The X-ray diffraction pattern of this precipitate does not show well-defined peaks, indicating it is an amorphous solid (Fig. 3). However, the sample (Fig. 3) does show broad humps centered around 3.31, 2.67, and 1.76 Å that cor-

Fig. 3 X-ray diffraction pattern using CuKα radiation of the sample precipitated from a 0.056 mol·dm^{-3} SnCl$_4$ solution equilibrated for 14 days at pH $= 0.76$. The solid phase is identified as SnO$_2$(am) (see text for details)
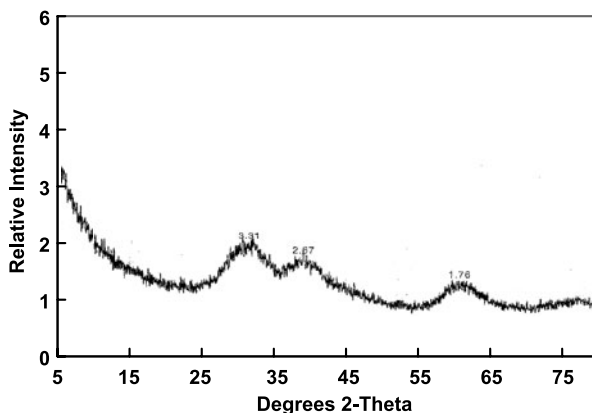
respond to major peaks for cassiterite. We therefore designate the precipitate as SnO$_2$(am). Amaya et al. [2] approached the solubility from the oversaturation direction and noticed that SnO$_2$(am) was present in samples that were equilibrated for 180 days. These data show that although freshly precipitated SnO$_2$ solids show broad peaks at regions where the major peaks for SnO$_2$(cr) are observed (Fig. 3), it apparently will take much longer than 180 days to approach SnO$_2$(cr) equilibrium from the oversaturation direction. Therefore, no attempt was made to conduct the study from the oversaturation direction. However, to effectively interpret solubility data, what is important is to be sure that the chemical potential of the solid phase is invariant during the time frame of investigations as indicated by the steady state conditions noticed in this study. In addition, as we will discuss later, the solubility product calculated from our data is similar to the previously estimated value (Wagman et al. [7]), showing that the steady state concentration noted in our study can be considered to represent equilibrium conditions.

3.2 Thermodynamic Interpretations of SnO$_2$(cr) Solubility Data (pH $< \sim$11.7)

HCl was used to adjust pH values in the low pH region which resulted in chloride concentrations that decrease approximately logarithmically with the increase in pH and that vary from 1.0 mol·dm^{-3} to very low levels (see Appendix Table 6). Therefore to accurately interpret the solubility data, reliable values are required for the SIT ion interaction parameters for (Sn^{4+}, Cl$^-$) and SnCl$_4^{4-n}$ complexes if these complexes are present in significant concentrations in our system.

Reported information regarding chloride complexes is extremely limited [5, 22–25], and the availability of thermodynamic data at room temperatures is more limited still; no reliable values applicable to our study can be obtained from these data. The study by Fatouros et al. [22] was conducted at a very high ionic strength (6.6 mol·kg^{-1}), which is beyond the applicability of the SIT model for extrapolation of these data to zero ionic strength without which the significance of various complex species cannot be ascertained. The SnO$_2$(am) solubility study by Oda and Amaya [5] in the presence of 0.46 mol·dm^{-3} chloride was conducted at pH values between 7.6 and 8.2. They observed Sn(IV) concentrations that were not significantly different from those in the absence of chloride. No significant quantitative or qualitative conclusions can be drawn from this study because the measured Sn concentrations are at or near the detection limits and the calculated Sn^{4+} activities at these pH values are many orders of magnitude lower than the detection limits or the measured total Sn concentrations. Sherman et al.'s [25] study deals with the characterization of Sn(IV)–Cl complexes
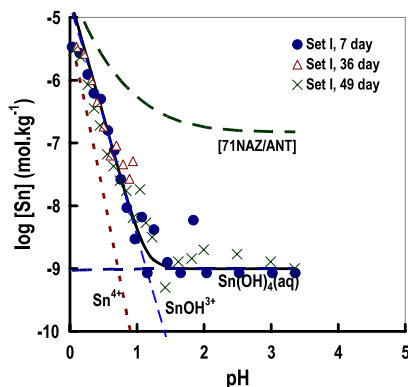
Fig. 4 Sn concentrations in filtrates (0.004 μm) from suspensions equilibrated with cassiterite ($SnO_2(cr)$) for different periods at pH values of <3.5. The *thick solid line* depicts total predicted Sn concentrations in equilibrium with cassiterite based on NONLINT-SIT calculations using the SIT based thermodynamic model (Tables 2 and 4) developed in this study; the other lines represent predicted concentrations of different species as identified. The *line* identified as [71NAZ/ANT] corresponds to predicted total Sn concentrations when the hydrolysis model of Nazarenko et al. [15] (Table 3) is used instead of the model developed in this study (see text for details)

Table 3 Values of the hydrolysis constants of Sn^{4+}, either reported ($\log_{10} K^c$) in Nazarenko et al. [15] for 1.04 $mol \cdot kg^{-1}$ or calculated ($\log_{10} K^0$) by us for zero ionic strength from their data

Reactions	$\log_{10} K^c$	[a]$\log_{10} K^0$
$Sn^{4+} + H_2O \rightleftharpoons SnOH^{3+} + H^+$	0.57	1.76
$Sn^{4+} + 2H_2O \rightleftharpoons Sn(OH)_2^{2+} + 2H^+$	0.68	2.66
$Sn^{4+} + 3H_2O \rightleftharpoons Sn(OH)_3^+ + 3H^+$	0.35	2.80
$Sn^{4+} + 4H_2O \rightleftharpoons Sn(OH)_4(aq) + 4H^+$	−0.87	1.56

[a]The $\log_{10} K^c$ values in 1.04 $mol \cdot kg^{-1}$ KNO_3 reported by Nazarenko et al. [15] were converted to zero ionic strength using the SIT model ($\log_{10} K^0 = \log_{10} K^c - \Delta Z^2 D + \Delta \varepsilon I_m$), where ΔZ^2 is the sum of valence squared of ions weighted by the stoichiometric coefficients of the products minus the reactants, I_m is the ionic strength in molality units, $D = (0.509(I_m)^{1/2})/(1 + 1.5(I_m)^{1/2})$ at 25 °C, and $\Delta \varepsilon$ is the difference between the sum of the ion interaction parameters weighted by the stoichiometric coefficients of the products minus the reactants. The SIT ion-interaction parameters used for these calculation were: $\varepsilon(H^+, NO_3^-) = 0.07$ from Rand et al. [14], and it was assumed that $\varepsilon(Sn^{4+}, NO_3^-) = 0.31$, $\varepsilon(SnOH^{3+}, NO_3^-) = 0.20$, $\varepsilon(Sn(OH)_2^{2+}, NO_3^-) = 0.10$, and $\varepsilon(Sn(OH)_3^+, NO_3^-) = 0.05$ are identical to the corresponding Th species as reported by Rand et al. [14]. These calculations also showed that by far the major correction factor in these calculated values is due to the Debye Huckel term rather than the ion-interaction term

using EXAFS. They report the formation of $SnCl_6^{2-}$ in a relatively high chloride concentration of 2.1 $mol \cdot dm^{-3}$, but report no thermodynamic data for this species. Migdisov and Williams-Jones [24] reported a high temperature (300–350 °C) study involving HCl-bearing water vapor and no data applicable to room temperature conditions are reported. Jackson and Helgeson [23], based on thermodynamic data for the Sn–Cl–OH system, report that Sn(IV)–OH species will control the solubility of $SnO_2(s)$ at high oxygen fugacities.

In the absence of specific reliable values for $SnCl_n^{4-n}$ complexes and because chloride concentrations in most of our samples are relatively low or zero (Tables 6 and 7), to interpret

Table 4 Values of equilibration constants for reactions involving Sn species evaluated in this study

Reaction	$\log_{10} K^0$	Reference
$SnO_2(cr) + 2H_2O \rightleftharpoons Sn^{4+} + 4OH^-$	-64.39 ± 0.30	This study[a]
$SnO_2(am) + 2H_2O \rightleftharpoons Sn^{4+} + 4OH^-$	-61.80 ± 0.29	This study[b]
$Sn^{4+} + H_2O \rightleftharpoons SnOH^{3+} + H^+$	1.86 ± 0.32	This study
$Sn^{4+} + 4H_2O \rightleftharpoons Sn(OH)_4(aq) + 4H^+$	≤ -0.62	This study
$Sn^{4+} + 5H_2O \rightleftharpoons Sn(OH)_5^- + 5H^+$	-9.20 ± 0.34	This study
$Sn^{4+} + 6H_2O \rightleftharpoons Sn(OH)_6^{2-} + 6H^+$	-20.28 ± 0.34	This study
$Na_2Sn(OH)_6(s) \rightleftharpoons Na_2Sn(OH)_6(aq)$	-5.29 ± 0.35	This study[c]
or		
$Na_2SnO_3(s) + 3H_2O \rightleftharpoons Na_2Sn(OH)_6(aq)$		

[a]The value is consistent with the value reported in Wagman et al. [7] and is nearly identical to the value (-64.5) listed in Feitknecht and Schindler [6]
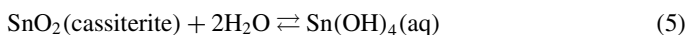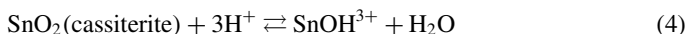
[b]Based on our interpretations of the data in Amaya et al. [2] and is similar to the value (-61.0) listed for the active solid in Feitknecht and Schindler [6]

[c]See the text for details

our data we used SIT ion-interaction parameters for different species involving Cl^- as listed in Table 2, which include $\varepsilon(H^+, Cl^-) = 0.12$ from Rand et al. [14] and assumed that the value for $\varepsilon(Sn^{4+}, Cl^-) = 0.25$ is identical to the value for $\varepsilon(Th^{4+}, Cl^-)$ reported in [14]. The assumption that $\varepsilon(Sn^{4+}, Cl^-) = \varepsilon(Th^{4+}, Cl^-)$ is reasonable because (1) both Sn and Th have the same charge, (2) Sn(IV) like Th(IV) forms very strong complexes with hydroxide, and (3) the chloride complexes/interactions with Th are rather weak, consistent with the Sn data at the chloride concentrations used in our study. The interpretation of Sn data discussed below shows that the dominant species in the low pH region (<2) is $SnOH^{3+}$, the only region where chloride concentration is highest in our study, indicating a slope of -3 whereas slopes of ≤ -4 would have been expected for this variable chloride concentration set had $SnCl_n^{4-n}$ been the dominant species.

3.2.1 Interpretations of Data at pH< ~3.5

NONLIN-SIT was used to interpret the solubility data. For these interpretations, we took a look first at Set I data at pH values $< {\sim}3.5$. Among the possible species (Sn^{4+}, $Sn(OH)_n^{4-n}$, $SnCl_n^{4-n}$) that can explain the data in this pH region, the best fits to the data were obtained using $SnOH^{3+}$ and $Sn(OH)_4^0$ as the dominant species along with using all of the appropriate ion-interaction parameters listed in Table 2. The modeling provided a $\log_{10} K^0$ of -6.52 ± 0.37 and $\leq -9.00 \pm 0.3$ for reactions (4 and 5), respectively. Since the Sn(IV) concentrations at pH values between 1.2 and 3.5 are at or near the detection limit, no reliable value for reaction 5 can be obtained from these data.

$$SnO_2(\text{cassiterite}) + 3H^+ \rightleftharpoons SnOH^{3+} + H_2O \tag{4}$$

$$SnO_2(\text{cassiterite}) + 2H_2O \rightleftharpoons Sn(OH)_4(aq) \tag{5}$$

Therefore, only an upper limit value for this reaction is reported. The predicted total Sn(IV) concentrations using this model are in close agreement with the experimental data (Fig. 4)

and show that there is no region of dominance of Sn^{4+} species. Assuming that Sn^{4+} becomes important at our lowest pH values, consistent with the observation that Sn^{4+} becomes important in >0.5 mol·dm^{-3} HCl solutions [12], and using the appropriate ion-interaction parameters (Table 2), to fit of the chemical potential of the solid phase such that the concentrations predicted by the species in reaction 4 are not significantly impacted, a $\log_{10} K^0 = -64.39 \pm 0.32$ was determined for reaction 6. The predicted concentrations using the model that included Sn^{4+} are in as close agreement with the experimental data as without these

$$SnO_2(\text{cassiterite}) + 2H_2O \rightleftarrows Sn^{4+} + 4OH^- \qquad (6)$$
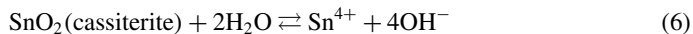
species and the overall uncertainty (0.32 versus 0.30) is similar in both cases (Fig. 4). Therefore, the calculated value for this reaction is reasonable and is similar to the estimated values reported in Feiknecht and Schindler [6] and Wagman et al. [7]. Combination of the solubility product of water with reactions 4 and 6, and reactions 5 and 6, provides $\log_{10} K^0 = 1.86 \pm 0.32$ for reaction 7 and ≤ -0.62 for reaction 8. No other data are available for comparison to these values other than those determined by Nazarenko et al. [15] (Table 3). There is a large degree of uncertainty

$$Sn^{4+} + H_2O \rightleftarrows SnOH^{3+} + H^+ \qquad (7)$$

$$Sn^{4+} + 4H_2O \rightleftarrows Sn(OH)_4(\text{aq}) + 4H^+ \qquad (8)$$
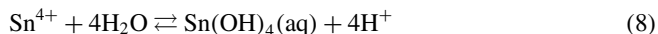
in the data reported by these authors because (1) the study was conducted in 1.04 mol·kg^{-1} KNO$_3$ solutions where the effects of nitrate complexation of Sn^{4+} cannot be evaluated, and (2) the values for $\varepsilon(Sn^{4+}, NO_3^-)$ and $\varepsilon(SnOH^{3+}, NO_3^-)$ for converting concentration constants to zero ionic strength are not available. If we assume that nitrate does not form significant complexes with Sn^{4+} and use the estimated values for ion-interaction parameters (Table 3): (1) the $\log_{10} K^0$ value estimated (1.76) from their data for reaction 7 is very similar to the value we determined (1.86), and (2) the estimated $\log_{10} K^0$ value of 1.56 for reaction 8 is over two orders of magnitude higher than the value we determined (≤ -0.62). In addition, using the $\log_{10} K^0$ values based on Nazarenko et al. [15] (Table 3) data in conjunction with (1) the solubility product of SnO$_2$(cassiterite) determined from our study and (2) the estimated[3] SIT ion-interaction parameters for $Sn(OH)_n^{4-n}$ species with chloride to predict Sn(IV) concentrations for our system, the calculated dominant species is not the SnOH^{3+} as we determined, and the total predicted concentrations are up to several orders of magnitude higher than observed by us (Fig. 4). These analyses indicate that it must just be coincidental that the calculated $\log_{10} K^0$ value (1.76) for reaction 7 from Nazarenko et al.'s [15] data is similar to the value (1.86 ± 0.32) we obtained; their overall model is drastically inconsistent with our extensive experimental data.

3.2.2 Interpretations of Data at pH ∼ 3.5 to 11.7

The observed Sn(IV) concentrations at pH values between about 3.5 and 8 are at or near the detection limit of Sn and are similar to the data between pHs of about 1.2 and 3.5.

---

[3]The SIT ion interaction parameter values in kg·mol^{-1} for $\varepsilon(Sn^{4+}, Cl^-) = 0.25$, $\varepsilon(SnOH^{3+}, Cl^-) = 0.19$, $\varepsilon(Sn(OH)_2^{2+}, Cl^-) = 0.13$, and $\varepsilon(Sn(OH)_3^-, Cl^-) = 0.06$, are the same as for the corresponding Th species as reported in Rand et al. [14].

However at pH values $> \sim 8$, there is a dramatic increase in Sn concentrations with increase in pH. This increase in Sn concentrations in equilibrium with $SnO_2(cr)$ must result from the formation of anionic complexes of Sn (e.g., $Sn(OH)_5^-$, and $Sn(OH)_6^{2-}$). Macchi and Pettine [16], using DPASV, reported the formation of $SnO(OH)_3^-$ (which can alternatively be written as $Sn(OH)_5^-$) at pH values >8, but reported no value for the complexation constant. Amaya et al. [2], with the same data also reported in Oda and Amaya [5], from extensive data on the solubility of $SnO_2(am)$ in 0.1 mol·dm^{-3} NaClO$_4$ reported the formation of $Sn(OH)_4(aq)$ at pH values of $< \sim 8$ and the formation of $Sn(OH)_5^-$, and $Sn(OH)_6^{2-}$ species at pH values $> \sim 8$. They reported $\log_{10} K^0 = -7.97$ for the reaction $[Sn(OH)_4(aq) + H_2O \rightleftharpoons Sn(OH)_5^- + H^+]$ and -18.38 for the reaction $[Sn(OH)_4(aq) + 2H_2O \rightleftharpoons Sn(OH)_6^{2-} + 2H^+]$. Since these values are based on equilibrium with $Sn(OH)_4(aq)$, the concentration of which in turn is dependent on detection limit values for Sn(IV) concentrations in equilibrium with $SnO_2(am)$, it stands to reason that the reported values cannot be considered reliable. However, that study was well done and the authors have reported all of their data. Therefore, it is possible to reinterpret the data of Amaya et al. [2] together with the data we have developed in order to develop a more comprehensive model consistent with the entire sets of available data.

The NONLINT-SIT approach that included the $\Delta_f G_m^\circ / RT$ value for Sn^{4+} from Wagman et al. [7] combined with the corresponding values for SnO_2(cassiterite), $Sn(OH)_4(aq)$, and $SnOH^{3+}$ based on the above reported complexation constants, were used to fit the $\Delta_f G_m^\circ / RT$ values for $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ from the SnO_2(cassiterite) solubility data in the pH range from approximately 6 to 11.7. Although the ionic strength of our solutions is very low in this pH region (varying between nearly zero to 0.003 mol·dm^{-3}), reasonable values for $\varepsilon(Na^+, Sn(OH)_5^-)$ and $\varepsilon(Na^+, Sn(OH)_6^{2-})$ (see Table 2) were included to interpret these data. These calculations provided $\log_{10} K^0$ values of -9.20 ± 0.34 and -20.28 ± 0.34 for the reactions 9 and 10, respectively. No other data are available for comparisons to these values.

$$Sn^{4+} + 5H_2O \rightleftharpoons Sn(OH)_5^- + 5H^+ \tag{9}$$

$$Sn^{4+} + 6H_2O \rightleftharpoons Sn(OH)_6^{2-} + 6H^+ \tag{10}$$
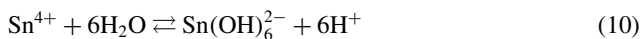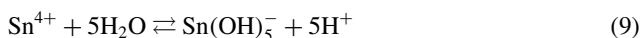
The Sn(IV) concentrations predicted using this model agreed closely with experimental Sn(IV) concentrations (Fig. 2) in the pH < 11.7 region.

The reliability of the model developed in this study was tested against the $SnO_2(am)$ solubility data of Amaya et al. [2]. For this testing, the thermodynamic data listed in Tables 2 and 4 for the aqueous Sn(IV) species were used to fit the chemical potential of $SnO_2(am)$, which provided a $\log_{10} K^0$ value of -61.80 ± 0.29 for the reaction 11. The predicted Sn(IV) concentrations from the aqueous phase model discussed above in combination with the

$$SnO_2(am) + 2H_2O \rightleftharpoons Sn^{4+} + 4OH^- \tag{11}$$

solubility product of $SnO_2(am)$ agreed closely with the experimental solubility data reported in Amaya et al. [2] and the two data points obtained in this study (Fig. 5); the data point at pH $= 0.76$ is the only value available for equilibrium with $SnO_2(am)$ (Fig. 3) in the low pH region. This close agreement of predicted and experimental data in the extensive pH region (0.76 to 11.7) lends credence to the reliability of the model developed in the present study. No value for reaction 11 was reported in Amaya et al. [2] for com-

Fig. 5 Experimental data obtained in this study and those reported by Amaya et al. [2] for the solubility of $SnO_2(am)$. *Lines* represent predicted concentrations (for 0.1 mol·dm^{-3} $NaClO_4$ at pH values >2 and for 0.22 mol·dm^{-3} chloride at pH values <2) based on the thermodynamic model (Tables 2 and 4) developed in this study: the *thick solid line* depicts total predicted Sn concentrations and the other lines the concentrations of different species as identified
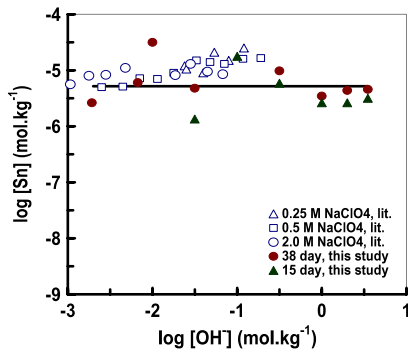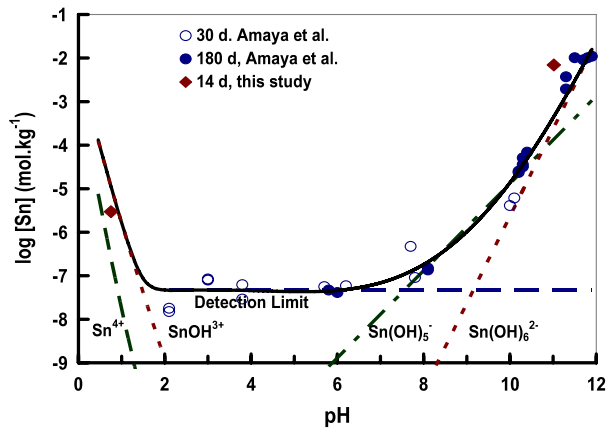

Fig. 6 Sn concentrations in filtrates (0.004 μm) from suspensions as a function of hydroxide equilibrated for different periods in equilibrium with $Na_2Sn(OH)_6(s)$ or $Na_2SnO_3(s)$ (see text for details). This study's experimental data are in NaOH and the "lit" marked data are in $NaClO_4$ solutions from Lothenbach et al. [26]. The *thick solid line* depicts total predicted Sn concentrations, for the experimental data of this study in equilibrium with this solid phase, using the thermodynamic model described in Tables 2 and 4

parisons, but the $\log_{10} K^0$ value determined in this study is similar to the value (-61) reported by Feitknecht and Schindler [6] for the solubility product of $SnO_2(\text{active})$, presumably $SnO_2(am)$.

3.3 Thermodynamic Interpretations of Solubility Data at pH > ~11.7

Although there is some scatter in the data, the observed Sn(IV) concentrations are nearly constant as a function of $\log_{10}[OH^-]$ (Fig. 6) with hydroxide concentrations varying between those that correspond to pH = 11.7 and 3.5 mol·dm^{-3} NaOH. No reaction involving $SnO_2(\text{cassiterite})$ can be written that can explain this behavior in this pH/OH region. Therefore, the solubility-controlling solid phase at this hydroxide range must be some solid other than $SnO_2(\text{cassiterite})$. The difference among the solutions at pH values <11.7 and those >11.7 is the increased amount of NaOH. Therefore, it is most likely that the solubility-controlling solid in the pH range >11.7 is the double salt (e.g. $SnO_2 \cdot 2NaOH$, which with additional two waters of hydration can be written as $Na_2Sn(OH)_6(cr)$ or as $Na_2SnO_3(cr)$ with

**Table 5** Calculated slopes of $\log_{10}$ [Sn] versus $\log_{10}$ [NaOH] for various reactions involving crystalline Na–Sn–hydroxide solids

Reaction	Slope[a]	Final estimated slope[b]
$Na_2Sn(OH)_6(cr) \rightleftarrows Na_2Sn(OH)_6(aq)$	0.0	0.0
$Na_2Sn(OH)_6(cr) \rightleftarrows NaSn(OH)_6^- + Na^+$	−1.0	−0.82
$Na_2Sn(OH)_6(cr) \rightleftarrows Sn(OH)_6^{2-} + 2Na^+$	−2.0	−1.5
$Na_2SnO_3(cr) + 3H_2O \rightleftarrows Na_2Sn(OH)_6(aq)$	0.0	0.0
$Na_2SnO_3(cr) + 3H_2O \rightleftarrows NaSn(OH)_6^- + Na^+$	−1.0	−0.82
$Na_2SnO_3(cr) + 3H_2O \rightleftarrows Sn(OH)_6^{2-} + 2Na^+$	−2.0	−1.5
$Na_2Sn_2O_5(cr) + 5H_2O + 2Na^+ + 2OH^- \rightleftarrows 2Na_2Sn(OH)_6(aq)$	2.0	1.62
$Na_2Sn_2O_5(cr) + 5H_2O + 2OH^- \rightleftarrows 2NaSn(OH)_6^-$	1.0	1.0
$Na_2Sn_2O_5(cr) + 5H_2O + 2OH^- \rightleftarrows 2Sn(OH)_6^{2-} + 2Na^+$	0.0	0.38
$Na_4SnO_4(cr) + 4H_2O \rightleftarrows Na_2Sn(OH)_6(aq) + 2Na^+ + 2OH^-$	−4.0	−3.62
$Na_4SnO_4(cr) + 4H_2O \rightleftarrows NaSn(OH)_6^- + 3Na^+ + 2OH^-$	−5.0	−4.44
$Na_4SnO_4(cr) + 4H_2O \rightleftarrows Sn(OH)_6^{2-} + 4Na^+ + 2OH^-$	−6.0	−5.06

[a]Slope of the given reaction for $\log_{10}$ [Sn] versus $\log_{10}$ [NaOH]

[b]Slopes in column 3 based on the listed reactions were corrected assuming that the corrections to $\log_{10} K^c$ due to the increase in ionic strength are all represented by changes in Sn(IV) concentrations. These corrections were estimated from [$\log_{10} K^c = \log_{10} K^0 + \Delta Z^2 D - \Delta\varepsilon I_m$] where the various quantities are defined in footnote "a" of Table 3, and the required ε values in addition to $\varepsilon(Na^+, NaSn(OH)_6^-) = -0.08$, which was assumed to be the same as for $\varepsilon(Na^+, Sn(OH)_5^-)$, are reported in Table 2

removal of one water molecule). The International Center for Diffraction Data (ICDD) lists a number of Na–Sn–hydroxide compounds [$Na_2Sn(OH)_6(cr)$, $Na_2SnO_3(cr)$, $Na_2Sn_2O_5(cr)$, and $Na_4SnO_4(cr)$] and it is a priori difficult, especially considering that definitive identification of the solid phase based on XRD was not possible, to determine which of these solid phases might be solubility-controlling in our system. In order to determine the most plausible solid(s) in our system we wrote solubility reactions of all of these solids involving different expected dominant aqueous species of Sn(IV) [$Na_2Sn(OH)_6(aq)$, $NaSn(OH)_6^-$, and $Sn(OH)_6^{2-}$] in the highly alkaline region to determine the slopes of the $\log_{10}$ [Sn] versus $\log_{10}$ [NaOH] plots, and compared them to the experimental values (Table 5). Since the slope in our experimental data is nearly zero, based on these slope analyses the solid that has these attributes is $Na_2Sn(OH)_6(s)$[4] or the dehydrated form of this solid ($Na_2SnO_3(s)$) when the solubility reaction involves the $Na_2Sn(OH)_6(aq)$ species. Based on this information, the $\log_{10} K^0 = -5.29 \pm 0.35$ for reaction 12 or 13[5] was calculated using the

$$Na_2Sn(OH)_6(s) \rightleftarrows Na_2Sn(OH)_6(aq) \qquad (12)$$
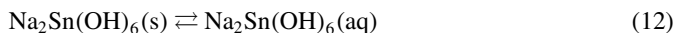
[4]Based on XRD data (Fig. 1), the solid is most likely crystalline. However, because of the difficulties in exactly matching the pattern with the patterns for the crystalline solids reported in ICDD [21], we opted to designate this solid simply as (s) rather than as (cr) for crystalline.

[5]Although the observed aqueous Sn(IV) behavior could also be explained by the reaction ($NaSn(OH)_5(s) \rightleftarrows NaSn(OH)_5(aq)$), it was not considered any further because no sodium solids of $Sn(OH)_5^-$ are reported in the literature.

$$Na_2SnO_3(s) + 3H_2O \rightleftharpoons Na_2Sn(OH)_6(aq) \tag{13}$$
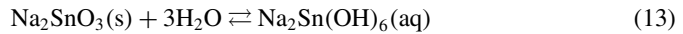
NONLINT-SIT code. There is close agreement between the predicted concentrations based on the above thermodynamic data and the experimental data in the high hydroxide concentration region (Fig. 6). Although there is this close agreement and these data can be used to predict Sn(IV) behavior in the highly alkaline region, additional studies involving well-characterized solids will be required to yield definitive thermodynamic data for this system.

No solubility data are available for any of the Na–Sn–hydroxide solids for comparisons. However, Lothenbach et al. [26] present data for the solubility of $CaSn(OH)_6(cr)$, as a function of hydroxide concentration ranging from 0.001 to 0.2 mol·dm^{-3}, and in $NaClO_4$ solutions of 0.25, 0.5, and 2.0 mol·dm^{-3}. Their calculations show, consistent with our data, that SnO_2(cassiterite), depending on Ca(II) concentration, is not stable in the highly alkaline region. They interpreted their data using the solubility reaction $(CaSn(OH)_6(cr) \rightleftharpoons Sn(OH)_6^- + Ca^{2+})$. Although there is a little scatter in their data, the measured Sn(IV) concentrations appear similar in all of the solutions and they report no analytical values for Ca(II) concentrations but have assumed them to be the same as Sn(IV) ($\sim 10^{-5}$). Their data could also have been interpreted very well assuming the reaction $(CaSn(OH)_6(cr) \rightleftharpoons CaSn(OH)_6(aq)$ which will show minimal dependence on ionic strength. If one assumes that the reaction they proposed is correct, then the Debye–Hückel and activity corrections would dictate that the $\log_{10} K$ they measured in 2.0 mol·dm^{-3} $NaClO_4$ solutions should have been about 0.7 log units higher than the one that they measured in 0.25 mol·dm^{-3} $NaClO_4$, inconsistent with their proposed reaction and their experimental data. Aside from these comments, their measured Sn concentrations (deciphered from the graph presented in their paper), although slightly higher, are very similar to the values we measure in our NaOH system (Fig. 6). This similarity, especially considering that their study was conducted in the presence of high concentrations of Na, shows that either (1) the solubilities of $CaSn(OH)_6(cr)$ and $Na_2Sn(OH)_6(s)$ are similar, or (2) $Na_2Sn(OH)_6(s)$ has a higher solubility than $CaSn(OH)_6(cr)$ and a small amount of $Na_2Sn(OH)_6(s)$ may have precipitated in their system which could have controlled the solubility.

4 Conclusion

The data shows that SnO_2(cr) at pH values of $< \sim 11.7$, and a double salt of NaOH and SnO_2 (e.g., $Na_2Sn(OH)_6(s)$) at pH values $> \sim 11.7$, are the stable phases. The extensive data made it possible to calculate reliable values of solubility products for SnO_2(cr), $Na_2Sn(OH)_6(s)$, and SnO_2(am) and equilibrium constants for the formation of $Sn(OH)_n^{4-n}$ with values of "n" equal to 1, 4, 5, and 6. Sn(IV) does not appear to form strong complexes with chloride. The extensive data with chloride concentrations varying up to 1.0 mol·dm^{-3} can be interpreted using existing SIT ion-interaction parameters (see text for details).

Appendix

Table 6 Sn concentrations in filtrates (0.004 μm) from suspensions equilibrated with cassiterite (SnO_2) for different timeperiods (Set I)

Sample No.	HCl/ mol·dm^{-3}	Equilibration periods					
		7 Day[a]		36 Day[a]		49 Day[a]	
		pH	$\log_{10}$ Sn	pH	$\log_{10}$ Sn	pH	$\log_{10}$ Sn
101	1.0000	0.033	−5.47	0.098	−5.47	0.053	−5.53
102	0.7943	0.145	−5.57	0.207	−5.58	0.157	−5.63
103	0.6310	0.266	−5.91	0.318	−6.00	0.265	−6.07
104	0.5012	0.356	−6.21	0.405	−6.35	0.359	−6.45
105	0.3981	0.458	−6.30	0.501	−6.74	0.447	−6.72
106	0.3162	0.566	−6.80	0.603	−7.20	0.555	−7.18
107	0.2512	0.662	−7.12	0.693	−7.04	0.649	−7.37
108	0.1995	0.758	−7.58	0.792	−7.34	0.745	−7.60
109	0.1585	0.848	−8.03	0.888	−7.57	0.839	−7.76
110	0.1259	0.968	−8.53	0.938	−7.29	0.940	−8.19
111	0.1000	1.072	−8.18	1.055	−7.93	1.045	−7.74
112	0.0794	1.153	−9.07	1.129	−8.04	1.130	−8.27
113	0.0631	1.252	−8.38	1.243	−8.24	1.226	−8.50
114	0.0398	1.453	−8.90	1.426	−7.99	1.420	−9.30
115	0.0251	1.650	−9.07	1.627	−8.30	1.615	−8.89
116	0.0158	1.840	−8.23	1.824	−8.07	1.814	−8.84
117	0.0100	2.038	−9.07	2.017	−8.37	1.994	−8.70
118	0.0032	2.522	−9.07	2.505	NV	2.491	−8.77
119	0.0010	3.019	−9.07	3.011	−8.44	2.992	−8.89
120	0.0003	3.360	−9.07	3.361	−8.40	3.350	−9.00

[a]The ($\log_{10}$ Sn) detection limits for the 7-day, 36-day, and 49-day sets are approximately −9.0, −8.0, and −8.9, respectively. NV indicates that no value is available for the given sample

Table 7 Sn concentrations in filtrates (Amicon 0.004 μm, unless otherwise identified) from suspensions equilibrated with cassiterite (SnO_2) for different periods (Set II)

Sample No.	NaOH/ mol·dm^{-3}	15 Day	15 Day (syringe)[a]	22 Day (unfiltered)[a]	38 Day	
		$\log_{10}$ Sn	$\log_{10}$ Sn	$\log_{10}$ Sn	pH	$\log_{10}$ Sn
121					6.378	−9.11
122					7.832	−9.26
123					8.211	−9.07
124					8.601	−8.41
125					8.678	−8.53
126					8.865	−7.87

Table 7 (*Continued*)

Sample No.	NaOH/ mol·dm^{-3}	15 Day log$_{10}$ Sn	15 Day (syringe)[a] log$_{10}$ Sn	22 Day (unfiltered)[a] log$_{10}$ Sn	38 Day pH	38 Day log$_{10}$ Sn
127[b]				−6.41	9.516	−8.12
128[b]	0.0010			−6.78	10.652	−7.20
129[b]	0.0032	−5.60		−5.52	11.284	−5.58
130	0.0100	−5.30		−5.34	11.827	−5.22
131	0.0316	−5.78	−5.87	−5.87	12.281[c]	−5.32
132	0.1000	−4.69	−4.75	−4.79	12.878[c]	−4.50
133	0.3160	−5.05	−5.23	−5.17	13.357[d]	−5.01
134	1.0000	−5.54	−5.58	−5.68	13.836[d]	−5.46
135	3.5000	−5.41	−5.5	−5.56	14.434[d]	−5.34
136	2.0000	−5.43	−5.58	−5.61	14.150[d]	−5.36

[a]Syringe, discs cut off of the Amicon Centricon-30 filter used in syringe; unfiltered, centrifuged for 5000 rpm for 20 minutes

[b]The measured pH values of Samples 127, 128, and 129 for 15 day sampling were 9.590, 10.740, and 11.295, respectively, and as expected are very similar to the measured values at the 38 day period

[c]The pH values estimated from OH activities ($14 + \log_{10} a_{OH}$) determined from the input NaOH concentrations using the SIT model for these samples were 12.43 and 12.859 respectively and are similar to the measured values

[d]These values were calculated from OH activities as described in footnote "[c]"

References

1. Weast, R.C.: Handbook of Chemistry and Physics, 53rd. Chemical Rubber Company, Cleveland (1972)
2. Amaya, T., Chiba, T., Suzuki, K., Oda, C., Yoshikawa, H., Yui, M.: Solubility of Sn(IV) oxide in dilute NaClO$_4$ solution at ambient temperature. Mater. Res. Soc. Symp. Proc. **465**, 751–758 (1997)
3. Lothenbach, B., Ochs, M., Wanner, H., Yui, M.: Thermodynamic data for the speciation and solubility of Pd, Pb, Sn, Sb, Nd, and Bi in aqueous solutions. JNC TN8400 99-011. Japan Nuclear Cycle Development Institute (now Japan Atomic Energy Agency) (1999)
4. Seby, F., Potin-Gautier, M., Giffant, E., Donard, O.F.X.: A critical review of thermodynamic data for inorganic tin species. Geochim. Cosmochim. Acta **65**, 3041–3053 (2001)
5. Oda, C., Amaya, T.: Effects of ligands on the solubility of tin. Japanese Nuclear Cycle Development Institute (1998)
6. Feitknecht, W., Schindler, P.: Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure Appl. Chem. **1**, 130–199 (1963)
7. Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L.: The NBS tables of chemical thermodynamic properties: selected values for inorganic and C1 and C2 organic substances in SI units. J. Phys. Chem. Ref. Data **11**(2), 1–392 (1982)
8. Barsukov, V.L., Klintsova, A.P.: Solubility of cassiterite in water and aqueous NaOH at 25 °C. Geokhimiya **10**, 1268–1272 (1970)
9. Barybin, V.I., Sharygin, P.M., Gonchar, V.F., Moiseev, V.E.: Solubility of hydrated tin dioxide in water. Izv. Akad. Nauk SSSR, Neorg. Mater. **23**, 1162–1165 (1988)
10. Dadze, T.P., Sorokhin, V.I., Nekrasov, I.Y.: Solubility of SnO$_2$ in water and in aqueous solution of HCl HCl + KCl, and HNO$_3$ at 200–400 °C and 101.3 MPa. Geokhimiya **10**, 1482–1492 (1981)
11. Klintsova, A.P., Varsukov, V.L.: Solubility of cassiterite in water and in aqueous NaOH solution at elevated temperatures. Geokhimiya **5**, 701–709 (1973)
12. Huey, C.S., Tartar, H.V.: The stannous-stannic oxidation-reduction potential. J. Am. Chem. Soc. **56**, 2585–2588 (1934)
13. Rai, D., Moore, D.A., Felmy, A.R., Rosso, K.M., Bolton, H.J.: PuPO$_4$(cr, hyd.) solubility product and Pu^{3+} complexes with phosphate and ethylenediaminetetraacetic acid. J. Solution Chem. **39**, 778–807 (2010)

14. Rand, M.H., Fuger, J., Grenthe, I., Neck, V., Rai, D.: Chemical thermodynamics of thorium. Nuclear Energy Agency, Organization for Economic Co-Operation and Development (2008)
15. Nazarenko, V.A., Antonovich, V.P., Nevskaya, E.M.: Spectrophotometric determination of the hydrolysis constants of tin(IV) ions. Russ J. Inorg. Chem. **15**, 980–982 (1971)
16. Macchi, G., Pettine, M.: Voltammetric characterization and chemical behavior of inorganic tin in natural waters. Environ. Sci. Technol. **14**, 815–818 (1980)
17. Pourbaix, M.: Atlas of d'equilibres electrochimiques a 25 °C. Gauthier-Villars & Cie, Paris (1964)
18. Rai, D.: Solubility product of Pu(IV) hydrous oxide and equilibrium constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), and Pu(V)/Pu(VI) couples. Radiochim. Acta **35**, 97–108 (1984)
19. Felmy, A.R.: GMIN: A Computerized Chemical Equilibrium Model Using a Constrained Minimization of the Gibbs Free Energy. Pacific Northwest National Laboratory, Richland (1990)
20. Sterner, S.M., Felmy, A.R., Rustad, J.R., Pitzer, K.S.: Thermodynamic Analysis of Aqueous Solutions Using INSIGHT. Pacific Northwest National Laboratory, Richland (1997)
21. The Powder Diffraction File (PDF) International Center for Diffraction Data (ICDD). Newtown Square, PA (2011)
22. Fatouros, N., Rouelle, F., Chemla, M.: Influence de la formation de complexes chlorures sur la reduction electrochimique de Sn^{IV} en milieu perchloroique acide. J. Chim. Phys. Phys.-Chim. Biol. **75**, 477–483 (1978)
23. Jackson, K.J., Helgeson, H.C.: Chemical and thermodynamic constraints on the hydrothermal transport and deposition of tin: I. Calculation of the solubility of cassiterite at high pressures and temperatures. Geochim. Cosmochim. Acta **49**, 1–22 (1985)
24. Migdisov, A.A., Williams-Jones, A.E.: An experimental study of cassiterite solubility in HCl-bearing water vapour at temperatures up to 350 °C. Implications for tin ore formation. Chem. Geol. **217**, 29–40 (2005)
25. Sherman, D.M., Ragnarsdottir, K.V., Oelkers, E.H., Collins, C.R.: Speciation of tin (Sn^{2+} and Sn^{4+}) in aqueous Cl solutions from 25 °C to 350 °C: an in situ EXAFS study. Chem. Geol. **167**, 169–176 (2000)
26. Lothenbach, B., Ochs, M., Hager, D.: Thermodynamic data for the solubility of tin(IV) in aqueous cementitious environments. Radiochim. Acta **88**, 521–526 (2000)