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## Computer simulation of the low-molecular-weight inorganic species distribution of antimony(III) and antimony(V) in natural waters

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**Abstract**—Computer speciation models of antimony in aqueous, multicomponent solutions of environmental and biological interest have been developed. Antimony is an element of increasing environmental significance but one whose chemical speciation has not previously been modelled in any comprehensive way. The available thermodynamic data have been critically evaluated and entered into a thermodynamic database. The JESS suite of computer programs has been used to develop the thermodynamically-consistent mass balance equations used for modelling purposes. The calculated speciation distributions successfully account for some but not all key known properties of antimony in natural waters. It is believed that the main difference is most likely due to kinetic factors. Copyright © 2003 Elsevier Ltd

### 1. INTRODUCTION

Antimony is a naturally-occurring element of industrial significance, especially through its growing role in fire retardants (Filella et al., 2002a). However, very little is known about the environmental behaviour of this element, in part because its speciation under natural water conditions has not hitherto been considered in any significant detail. In this study, we develop chemical speciation models for antimony in a number of selected multicomponent aqueous solutions of environmental interest. We seek to establish for the first time a working description of antimony in aqueous, multicomponent media involving its different oxidation states and its most important interactions with relevant low-molecular-weight (l.m.w.) ligands. Our aim is to provide a better, more coherent basis for future experimental investigations of antimony geochemistry, biochemistry and toxicology.

For this purpose we have used the JESS (Joint Expert Speciation System) modelling package, version 6.4 (May and Murray, 2000). This computer software is designed to process thermodynamic data for chemical reactions so as to achieve thermodynamic consistency automatically. It attempts to deal with the serious discrepancies that often occur between published equilibrium constants, allowing a consistent set of mass balance equations for chemical speciation modelling to be produced by systematic means.

In this regard, antimony presents a considerable challenge, covering the entire range of issues that typically confront modellers of chemical speciation in environmental and biologic media. The available thermodynamic data are sparse and rarely measured under appropriate conditions of ionic strength and background electrolyte medium. Many values reported in supposedly critical compilations are just taken from the same few, sometimes very old, underlying sources of experimental measurements. Of particular concern are the errors that arise from the reporting of equilibrium constants measured in concen-

trated electrolyte solutions as (the best estimate of) the standard state (infinite dilution) value. However, there are several other kinds of serious data inadequacy. It is well known that ternary (or mixed ligand) species are often important in multicomponent electrolyte solutions but there are, to our knowledge, no reported equilibrium constants whatsoever for such species involving antimony. In those few cases where measurements of binary systems have been performed under similar experimental conditions, some serious discrepancies are also evident. Evaluation of the measured values available from the literature is made considerably more difficult by the proliferation of chemical notations used to represent species that are thermodynamically identical in water, such as  $\text{SbO}_2^-$  and  $\text{Sb}(\text{OH})_4^-$ ; this appears, for example, to have confused the compilers of at least one widely-used speciation code (U.S. Environmental Protection Agency, 1999). Finally, there are important kinetic constraints between certain species that need to be taken into account when modelling antimony solution chemistry.

### 2. MODELLING PROCEDURE

JESS is a large suite of software, comprising many independent computer programs. These provide various tools for modelling aqueous solution chemical speciation in complex systems, which differ significantly from other speciation packages. In particular this is because (1) the thermodynamic parameters appear in its database just as they appear in the literature, i.e., in their raw form, without redundancies or inconsistencies being omitted and with minimal human transformation; (2) reactions, and their equilibrium constants, are represented symbolically in different ways at different stages in the procedure to enhance numerical stability and to minimize error propagation; and (3) JESS has a capability for dealing with systems that only attain a metastable, 'quasi-equilibrium'. Details about the aims and methods of JESS can be found on the World Wide Web (<http://jess.murdoch.edu.au/>) and in several papers (May and Murray, 1991a, 1991b, 2000; May, 2000; Filella et al., 2001).

In essence, JESS modelling is accomplished by a sequence of operations. First, the data are extracted from the 'Parent'

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database (<http://jess.murdoch.edu.au/>). Secondly, they are assessed and combined to obtain the best possible estimates for the parameters of the thermodynamic functions for all species. Thirdly, they are transformed by gaussian elimination into a consistent set of mass balance equations and, finally, they are solved for particular conditions of temperature, electrolyte medium and ionic strength (May and Murray, 2000).

In JESS, the evaluation of equilibrium constants is thus achieved by an entirely generic approach in which *all* the constants known for each reaction are taken into account. After each individual thermodynamic parameter value has been assessed (weighted) and entered into the database, the procedure for achieving internal thermodynamic consistency is entirely automatic. This allows for systematic averaging of equilibrium constants, error-free transformation of reactions and objective elimination of all redundancies.

JESS uses empirical functions of a Debye-Hückel type to describe how the equilibrium constants vary as a function of ionic strength and temperature (May, 2000). The parameters in these functions are called Unconditional Correction Constants (UCCs). For each reaction present in the database, the smoothing functions are preevaluated and their UCCs then stored in the database itself. The functions used by JESS have been shown to describe adequately how the equilibrium constants of a wide variety of reactions vary with the changes in conditions to high ionic strengths and temperatures (May, 2000; Filella et al., 2001).

### 3. RESULTS

The sparsity of data for antimony is striking. Only the antimony-sulfur system has been the subject of recent systematic study, mainly in relation to the role of such species in hydrothermal systems (Ritchie, 1961; Stauffer and Thompson, 1984; Krupp, 1988; Spycher and Reed, 1989). This lack of data is, in part, because both Sb(III) and Sb(V) ions hydrolyse readily in aqueous solution, thus making it difficult to determine the concentrations of 'free' antimony ions in solution except in highly acidic or basic media or in very dilute solutions. It is noteworthy that, because of such analytical limitations, experimental data for antimony systems have often been collected under supersaturated conditions (i.e., favouring precipitation), whereas there is no evidence for precipitation of antimony under the highly dilute conditions of natural waters.

The first step in the establishment of the antimony model has been the collection of all stability constant data available and the subsequent JESS UCC evaluation. To decrease error propagation, direct sources have been preferred and multi-referencing of identical primary values avoided. All species for which equilibrium constants have been found are listed in Table 1; their published associated equilibrium constant values are given in the Appendix in the form used by their authors. Thermochemical values needed for temperature corrections have also been included in the database, our main source being Barin and Platzki (1995). However, it is evident that for the present purpose these data are far from complete and do not contain much information relevant to any but the most dilute systems, at best.

In the establishment of any speciation model, the second step

Table 1. Antimony species included in published equilibrium studies.

$\text{Sb}^{3+}$	$\text{Sb}_2\text{O}_5(\text{s})$
$\text{Sb}(\text{OH})^{2+}$	$\text{Sb}_2\text{O}_4(\text{s})$
$\text{Sb}(\text{OH})_2^+$	$\text{Sb}(\text{s})$
$\text{Sb}(\text{OH})_3^0$	$\text{SbH}_3(\text{g})$
$\text{Sb}(\text{OH})_4^-$	$\text{SbCl}^{2+}$
$\text{Sb}_2(\text{OH})_2^{4+}$	$\text{SbCl}_2^+$
$\text{Sb}^{5+}$	$\text{SbCl}_3^0$
$\text{Sb}(\text{OH})_4^+$	$\text{SbCl}_4^-$
$\text{Sb}(\text{OH})_5^0$	$\text{SbCl}_5^{2-}$
$\text{Sb}(\text{OH})_6^-$	$\text{SbCl}_6^{3-}$
$\text{Sb}_{12}\text{H}_4(\text{OH})_{72}^{8-}$	$\text{SbCl}_3(\text{s})$
$\text{Sb}_{12}\text{H}_5(\text{OH})_{72}^{7-}$	$\text{SbCl}_3\text{OH}^-$
$\text{Sb}_{12}\text{H}_6(\text{OH})_{72}^{6-}$	$\text{SbCl}_3(\text{OH})_3^-$
$\text{Sb}_{12}\text{H}_7(\text{OH})_{72}^{5-}$	$\text{SbCl}_4(\text{OH})_2^-$
$\text{Sb}_{12}\text{H}_8(\text{OH})_{72}^{4-}$	$\text{SbCl}_5\text{OH}^-$
$\text{Sb}_{12}\text{H}_9(\text{OH})_{72}^{3-}$	$\text{SbCl}_6^-$
$\text{Sb}_{12}(\text{OH})_{64}^{4-}$	$\text{SbS}_2^-$
$\text{Sb}_{12}(\text{OH})_{65}^{5-}$	$\text{SbS}_3^{3-}$
$\text{Sb}_{12}(\text{OH})_{66}^{6-}$	$\text{Sb}_2\text{S}_4^{2-}$
$\text{Sb}_{12}(\text{OH})_{67}^{7-}$	$\text{Sb}_2\text{HS}_4^-$
$\text{Sb}_2\text{O}_3(\text{s})$	$\text{Sb}_2\text{H}_2\text{S}_4^0$
$\text{SbOOH}(\text{s})$	$\text{Sb}_2\text{S}_3(\text{s})$
$\text{Sb}_2\text{O}_3(\text{cubic},\text{s})$	$\text{SbS}(\text{OH})_2^-$
$\text{Sb}_2\text{O}_3(\text{rhombic},\text{s})$	$\text{Sb}_2\text{S}_2(\text{OH})_3^0$
$\text{Sb}_4\text{O}_6(\text{s})$	$\text{Sb}_4\text{S}_7^{2-}$
$\text{Sb}_4\text{O}_6(\text{rhombic},\text{s})$	$\text{SbS}_4^{3-}$
$\text{Sb}_4\text{O}_6(\text{cubic},\text{s})$	

is the determination of a set of 'basis species'. This is the smallest set of species in terms of which all other species can be expressed via reactions. The criteria for preferring one set of basis species over another are complicated. Although the results of speciation modelling ought in principle not to depend on how the equations are set up, this is often not the case in practice. Two interrelated reasons for this are: (1) differences in the way errors propagate; and (2) differences in numerical behaviour when the equations are being solved. Often there is a trade-off necessary between avoiding convergence problems, by choosing as basis species the most predominant ones, and minimising the effect of experimental errors in the equilibrium constants by using the species that give the best linear combination results. In this work, both criteria were considered and  $\text{Sb}(\text{OH})_3^0$  has been selected as the most appropriate basis species for antimony in the present context.

JESS establishes all the linear combinations needed to define the stability of all other species relative to the basis species. The task is accomplished by a gaussian elimination procedure that works through all the available reactions and determines which is judged likely to yield the best linear combinations of reac-

tions for each non-basis species. Results obtained for the antimony systems are shown in Tables 2 to 4 for 25°C and 0 mol/L ionic strength. UCCs are simultaneously obtained for each linear combination of reactions that determines the concentration of a species from the concentration of the basis species. Each set of UCC parameters are associated with scores that indicate how well the UCC spans the ranges of ionic strength and temperatures specified. These scores are used in the selection of the best linear combinations of reactions. Any other auxiliary constant data needed for a number of reactions (see Tables 2–4) have been taken from JESS database. Construction of the model including antimony, chloride, fluoride and sulfide in aqueous solution involved using a data set with 1597 equilibrium constants, 133 Gibbs energy values, 118 standard potentials and 446 enthalpy values.

Through the procedure of calculation of the linear combinations, JESS helps with the systematic tracking and elimination (when possible) of inconsistencies in the database. Two main procedures have been of particular use in the present case: (1) comparison of data to determine which of the inconsistent values are likely to be the least accurate; (2) transmission of information, usually about the effects of ionic strength, from reactions with measured values to those without them. Both of these procedures tend to be tedious and time-consuming but have been greatly alleviated by the automated computational procedure. A critical appraisal of existing thermodynamic data obtained by application of the described procedure is summarised below.

### 3.1. Redox Potentials

Antimony can exist in a variety of oxidation states (–III, 0, III, V) but in biologic and environmental systems it is usually found in only two, most commonly as Sb(V) in oxic aquatic systems but also as Sb(III) in oxygen-depleted media. However, on account of its multiple oxidation states, antimony can participate in a wide variety of redox couples. Few experimental measurements of redox standard potentials exist in the literature (Grube and Schweigardt, 1923; Schuhmann, 1924; Brown and Swift, 1949; Vasil'ev and Shorokhova, 1972; Vasil'ev et al., 1973; Chazov, 1976) and some of them are very old. Some authors (Latimer, 1952; Pitman et al., 1957) calculated standard potentials from Gibbs energy values compiled by NBS. The Gibbs energies of formation of compounds used by Pitman et al. (1957) were essentially those recommended by Latimer (1952). Published values thus involve a large number of reactions (see Appendix, Table A2), including many different redox couples. Both experimental and calculated redox potential values have subsequently been included in compilations and critical reviews seemingly without further consideration of their validity or pedigree. Sometimes they are reported as values for infinite dilution even though they were originally determined at higher ionic strength. For example, Lide and Frederikse (1995) quote the value determined by Grube and Schweigardt (1923) at 20°C and  $I = 10$  mol/L NaOH for the reaction  $\text{Sb(OH)}_6^- + 2e^- = \text{Sb(OH)}_4^- + 2\text{OH}^-$ , as being applicable at 25°C and infinite dilution. The footnotes in Table A2 of the Appendix give further examples.

Our data analysis suggests that the values from Schuhmann

(1924), Brown and Swift (1949), Vasil'ev and Shorokhova (1972), Vasil'ev et al. (1973) (reaction  $\text{Sb[s]} + 4\text{OH}^- = \text{SbO}_2^- + 2\text{H}_2\text{O} + 3e^-$ ) and some of the potential values from Latimer (1952) (reactions:  $2\text{SbO}^+ + 3\text{H}_2\text{O} = \text{Sb}_2\text{O}_5(\text{s}) + 6\text{H}^+ + 4e^-$ ,  $\text{Sb}(\text{s}) + 3\text{H}^+ + 3e^- = \text{SbH}_3(\text{g})$ , and  $2\text{S}^{2-} + \text{SbS}_2^- = \text{SbS}_4^{3-} + 2e^-$ ) are thermodynamically consistent with the other available chemical reactions. UCC extrapolation of redox potentials determined by Grube and Schweigardt (1923) in the presence of different concentrations of NaOH for the reaction  $\text{Sb(OH)}_6^- + 2e^- = \text{Sb(OH)}_4^- + 2\text{OH}^-$  did not give a consistent value at infinite dilution conditions and the value was therefore calculated instead by linear combination of other reactions. Pitman et al. (1957), Vasil'ev et al. (1973) (reaction  $4\text{Sb}(\text{s}) + 12\text{OH}^- = \text{Sb}_4\text{O}_6(\text{s}) + 6\text{H}_2\text{O} + 12e^-$ ) and Chazov (1976) data were generally inconsistent with other reactions and, hence, they have not been included in the present model.

The redox reaction supposedly between  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$  reported by Brown and Swift (1949) was also excluded from the calculations. This study is difficult to relate to other measurements not only because it was made with very acidic solutions but also because no mention is made by these authors of any other antimony species in solution, which seems implausible. Moreover, some preliminary models in which the reaction was considered indicated that it would grossly overestimate the  $\text{Sb}^{5+}$  species concentration.

The redox couples studied often contained Sb(s) or a solid antimony (III) oxide as one of the species. Some discussion of issues related to the lack of an adequate characterisation of the antimony (III) oxide isotropic forms used in the experiments appears below.

### 3.2. Acid-Base Equilibria and Oxides Solubilities

Only one experimental study of Sb(V) acid-base equilibria could be found in the literature (Lefebvre and Maria, 1963). Their data were re-interpreted by Baes and Mesmer (1976) whose  $\text{p}K_a$  value has been cited more or less universally ever since. Baes and Mesmer (1976) also calculated a value for the solubility product of antimony(V) oxide from Tourky and Mousa (1948) solubility data and this value has remained the single point of reference.

Only a few acid-base studies have been published for Sb(III) acid-base equilibria (Kasper, 1941; Pavlov and Lazarov, 1958a, 1958b; Mishra and Gupta, 1968; Ahrland and Bovin, 1974; Shoji et al., 1974; Antonovich et al., 1977). Some measurements have been made in the context of solubility studies, which implies the complications of dealing properly with solid phases (Kasper, 1941; Ahrland and Bovin, 1974). Other methods used include polarography (Pavlov and Lazarov, 1958a, 1958b) and spectrophotometry with gallein as a competitive ligand allowing measurements to be made at Sb concentrations as low as  $10^{-5}$  mol/L (Antonovich et al., 1977). Particular mention should be made of the study by Shoji et al. (1974) who, by using a solvent extraction method combined with radiotracers, minimised hydrolysis by working only with trace concentrations of Sb ( $10^{-8}$  mol/L).

Antimony(III) oxide solubility has been the subject of attention for nearly 80 yr (Schuhmann, 1924; Bayerle, 1925; Gayer and Garrett, 1952; Kovalenko, 1958; Fridman et al., 1965;

Table 2. Best stability constant values for all antimony acid-base and oxide species. Linear combinations of the published reactions used in the calculation of the proposed values are also given.<sup>a</sup>

Reaction	$\log \beta^b$	Linear combination
$\text{Sb(OH)}_3^0 + 6\text{H}^+ + 6\text{e}^- = 3\text{H}_2\text{O} + \text{SbH}_3(\text{g})$	-13.62	(+) $1.5\text{H}_2(\text{g}) + \text{Sb}(\text{s}) = \text{SbH}_3(\text{g})$ (+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (+3) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$2\text{Sb(OH)}_3^0 = 3\text{H}_2\text{O} + \text{Sb}_2\text{O}_3(\text{s})$	8.480	(-2) $0.5\text{Sb}_2\text{O}_3(\text{s}) + 1.5\text{H}_2\text{O} = \text{Sb(OH)}_3^0$
$\text{Sb(OH)}_3^0 = \text{Sb(OH)}_3(\text{s})$	0.2327	(-) $\text{Sb(OH)}_3(\text{s}) = \text{Sb}^{3+} + 3\text{OH}^-$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{Sb(OH)}^{2+} + \text{H}^+$ (-) $\text{Sb(OH)}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-3) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$2\text{Sb(OH)}_3^0 = 3\text{H}_2\text{O} + \text{Sb}_2\text{O}_3(\text{cubic,s})$	11.44	(+) $2\text{Sb}(\text{s}) + 1.5\text{O}_2(\text{g}) = \text{Sb}_2\text{O}_3(\text{cubic,s})$ (+2) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (-3) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-3) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-2) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-3) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$2\text{Sb(OH)}_3^0 = 3\text{H}_2\text{O} + \text{Sb}_2\text{O}_3(\text{rhombic,s})$	10.00	(+) $2\text{Sb}(\text{s}) + 1.5\text{O}_2(\text{g}) = \text{Sb}_2\text{O}_3(\text{rhombic,s})$ (+2) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (-3) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-3) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-2) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-3) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$\text{Sb(OH)}_3^0 = \text{H}_2\text{O} + \text{SbOOH}(\text{s})$	4.371	(-) $\text{SbOOH}(\text{s}) + \text{H}_2\text{O} = \text{Sb}^3\text{OH}^- (2) + \text{OH}^-$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$2\text{Sb(OH)}_3^0 = 2\text{H}^+ + 2\text{e}^- + 2\text{H}_2\text{O} + \text{Sb}_2\text{O}_4(\text{s})$	-1.680	(+) $2\text{Sb}(\text{s}) + 2\text{O}_2(\text{g}) = \text{Sb}_2\text{O}_4(\text{s})$ (+2) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (-4) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-4) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-2) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-4) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$4\text{Sb(OH)}_3^0 = 6\text{H}_2\text{O} + \text{Sb}_4\text{O}_6(\text{s})$	18.53	(-) $\text{Sb}_4\text{O}_6(\text{s}) + 12\text{H}^+ + 12\text{e}^- = 4\text{Sb}(\text{s}) + 6\text{H}_2\text{O}$ (+4) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (-4) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$2\text{Sb(OH)}_3^0 = 4\text{e}^- + 4\text{H}^+ + \text{H}_2\text{O} + \text{Sb}_2\text{O}_5(\text{s})$	-37.26	(+) $2.5\text{O}_2(\text{g}) + 2\text{Sb}(\text{s}) = \text{Sb}_2\text{O}_5(\text{s})$ (+2) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb}(\text{s}) + 2\text{H}_2\text{O}$ (-5) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-5) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-2) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-5) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$4\text{Sb(OH)}_3^0 = 6\text{H}_2\text{O} + \text{Sb}_4\text{O}_6(\text{rhombic,s})$	17.71	(-) $\text{Sb}_4\text{O}_6(\text{rhombic,s}) + 8\text{H}^+ = 2\text{Sb}_2(\text{OH})_2^{4+} + 2\text{H}_2\text{O}$ (+2) $2\text{Sb(OH)}_2^+ + 2\text{H}^+ = \text{Sb}_2(\text{OH})_2^{4+} + 2\text{H}_2\text{O}$ (-4) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$4\text{Sb(OH)}_3^0 = 6\text{H}_2\text{O} + \text{Sb}_4\text{O}_6(\text{cubic,s})$	18.56	(-) $\text{Sb}_4\text{O}_6(\text{cubic,s}) + 8\text{H}^+ = 2\text{Sb}_2(\text{OH})_2^{4+} + 2\text{H}_2\text{O}$ (+2) $2\text{Sb(OH)}_2^+ + 2\text{H}^+ = \text{Sb}_2(\text{OH})_2^{4+} + 2\text{H}_2\text{O}$ (-4) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$

Table 2. continued

Reaction	$\log \beta^b$	Linear combination
$\text{Sb(OH)}_3^0 + 3\text{H}^+ + 3\text{e}^- = 3\text{H}_2\text{O} + \text{Sb(s)}$	12.26	(+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + 2\text{H}_2\text{O}$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{Sb}^{3+}$	-0.01864	(-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{Sb(OH)}^{2+} + \text{H}^+$ (-) $\text{Sb(OH)}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 2\text{H}^+ = 2\text{H}_2\text{O} + \text{Sb(OH)}^{2+}$	1.190	(-) $\text{Sb(OH)}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + \text{H}^+ = \text{H}_2\text{O} + \text{Sb(OH)}_2^+$	-1.371	$\text{Sb(OH)}_3^0 + \text{H}^+ = \text{H}_2\text{O} + \text{Sb(OH)}_2^+$
$2\text{Sb(OH)}_3^0 + 4\text{H}^+ = 4\text{H}_2\text{O} + \text{Sb}_2(\text{OH})_4^{4+}$	3.545	(+) $2\text{Sb(OH)}_2^+ + 2\text{H}^+ = \text{Sb}_2(\text{OH})_4^{4+} + 2\text{H}_2\text{O}$ (-2) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + \text{H}_2\text{O} = \text{H}^+ + \text{Sb(OH)}^-$	-11.70	(-0.25) $\text{Sb}_4\text{O}_6(\text{s}) + 12\text{H}^+ + 12\text{e}^- = 4\text{Sb(s)} + 6\text{H}_2\text{O}$ (+) $0.25\text{Sb}_4\text{O}_6(\text{s}) + 1.5\text{H}_2\text{O} + \text{OH}^- = \text{Sb(OH)}_4^-$ (+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + 2\text{H}_2\text{O}$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$\text{Sb(OH)}_3^0 + \text{H}_2\text{O} = 2\text{e}^- + \text{H}^+ + \text{Sb(OH)}_4^+$	-24.61	(+) $\text{Sb(OH)}_6^- + 2\text{H}^+ = \text{Sb(OH)}_4^+ + 2\text{H}_2\text{O}$ (+) $\text{Sb(OH)}_5^0 + \text{H}_2\text{O} = \text{Sb(OH)}_6^- + \text{H}^+$ (+) $0.5\text{Sb}_2\text{O}_5(\text{s}) + 2.5\text{H}_2\text{O} = \text{Sb(OH)}_5^0$ (+0.5) $2.5\text{O}_2(\text{g}) + 2\text{Sb(s)} = \text{Sb}_2\text{O}_5(\text{s})$ (+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + 2\text{H}_2\text{O}$ (-2.5) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-2.5) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-2.5) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$\text{Sb(OH)}_3^0 + 2\text{H}_2\text{O} = 2\text{e}^- + 2\text{H}^+ + \text{Sb(OH)}_5^0$	-22.33	(+) $0.5\text{Sb}_2\text{O}_5(\text{s}) + 2.5\text{H}_2\text{O} = \text{Sb(OH)}_5^0$ (+0.5) $2.5\text{O}_2(\text{g}) + 2\text{Sb(s)} = \text{Sb}_2\text{O}_5(\text{s})$ (+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + 2\text{H}_2\text{O}$ (-2.5) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-2.5) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-2.5) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$\text{Sb(OH)}_3^0 + 3\text{H}_2\text{O} = 2\text{e}^- + 3\text{H}^+ + \text{Sb(OH)}_6^-$	-25.15	(+) $\text{Sb(OH)}_5^0 + \text{H}_2\text{O} = \text{Sb(OH)}_6^- + \text{H}^+$ (+) $0.5\text{Sb}_2\text{O}_5(\text{s}) + 2.5\text{H}_2\text{O} = \text{Sb(OH)}_5^0$ (+0.5) $2.5\text{O}_2(\text{g}) + 2\text{Sb(s)} = \text{Sb}_2\text{O}_5(\text{s})$ (+) $\text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + 2\text{H}_2\text{O}$ (-2.5) $0.5\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) + \text{e}^- = \text{OH}^-$ (-2.5) $\text{H}^+ + \text{e}^- = 0.5\text{H}_2(\text{g})$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$ (-2.5) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$

<sup>a</sup> For polymeric species, only  $\log \beta$  is given:

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 32\text{H}^+ + \text{Sb}_{12}\text{H}_4(\text{OH})_{72}^{8-} \quad \log \beta = -342.2$$

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 31\text{H}^+ + \text{Sb}_{12}\text{H}_5(\text{OH})_{72}^{7-} \quad \log \beta = -347.0$$

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 30\text{H}^+ + \text{Sb}_{12}\text{H}_6(\text{OH})_{72}^{6-} \quad \log \beta = -350.7$$

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 29\text{H}^+ + \text{Sb}_{12}\text{H}_7(\text{OH})_{72}^{5-} \quad \log \beta = -353.3$$

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 28\text{H}^+ + \text{Sb}_{12}\text{H}_8(\text{OH})_{72}^{4-} \quad \log \beta = -354.7$$

$$36\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 27\text{H}^+ + \text{Sb}_{12}\text{H}_9(\text{OH})_{72}^{3-} \quad \log \beta = -355.1$$

$$28\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 28\text{H}^+ + \text{Sb}_{12}(\text{OH})_{64}^{4-} \quad \log \beta = -247.6$$

$$29\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 29\text{H}^+ + \text{Sb}_{12}(\text{OH})_{65}^{5-} \quad \log \beta = -251.2$$

$$30\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 30\text{H}^+ + \text{Sb}_{12}(\text{OH})_{66}^{6-} \quad \log \beta = -256.1$$

$$31\text{H}_2\text{O} + 12\text{Sb(OH)}_3^0 = 24\text{e}^- + 31\text{H}^+ + \text{Sb}_{12}(\text{OH})_{67}^{7-} \quad \log \beta = -261.9$$

<sup>b</sup> To avoid round-off errors, values are calculated and given to four significant figures; their accuracy is difficult to establish but typically will be 1 or 2 orders of magnitude worse than the stated precision.

Table 3. Best stability constant values for all antimony-chloride species. Linear combinations of the published reactions used in the calculation of the proposed values are also given.

Reaction	$\log \beta^a$	Linear combination
$\text{Sb(OH)}_3^0 + 6\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_6^{3-}$	6.986	(+) $\text{SbCl}_4^- + 2\text{Cl}^- = \text{SbCl}_6^{3-}$ (+) $3\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}_3^0$ (+) $\text{SbCl}_3^0 + \text{Cl}^- = \text{SbCl}_4^-$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 5\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_5^{2-}$	5.077	(+) $5\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}_5^{2-}$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 4\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_4^-$	7.981	(+) $3\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}_3^0$ (+) $\text{SbCl}_3^0 + \text{Cl}^- = \text{SbCl}_4^-$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 3\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_3^0$	5.981	(+) $3\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}_3^0$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 2\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_2^-$	3.319	(+) $2\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}_2^-$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + \text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}^{2+}$	3.331	(+) $\text{Cl}^- + \text{Sb}^{3+} = \text{SbCl}^{2+}$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{Sb(OH)}_3^0 + 3\text{Cl}^- + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbCl}_3(\text{s})$	0.2714	(-) $\text{SbCl}_3(\text{s}) + 2\text{H}_2\text{O} = \text{Sb(OH)}_2^+ + 2\text{H}^+ + 3\text{Cl}^-$ (-) $\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$
$\text{SbCl}_5\text{OH}^- + \text{Cl}^- + \text{H}^+ = \text{H}_2\text{O} + \text{SbCl}_6^-$	-4.321	$\text{SbCl}_5\text{OH}^- + \text{Cl}^- + \text{H}^+ = \text{H}_2\text{O} + \text{SbCl}_6^-$
$\text{SbCl}_5\text{OH}^- + \text{H}_2\text{O} = \text{Cl}^- + \text{H}^+ + \text{SbCl}_4(\text{OH})_2^-$	-3.501	$\text{SbCl}_5\text{OH}^- + \text{H}_2\text{O} = \text{Cl}^- + \text{H}^+ + \text{SbCl}_4(\text{OH})_2^-$
$\text{SbCl}_5\text{OH}^- + 2\text{H}_2\text{O} = 2\text{Cl}^- + 2\text{H}^+ + \text{SbCl}_3(\text{OH})_3^-$	6.612	(-) $\text{SbCl}_3(\text{OH})_3^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_4(\text{OH})_2^- + \text{H}_2\text{O}$  (-) $\text{Cl}^- + \text{H}^+ + \text{SbCl}_4(\text{OH})_2^- = \text{SbCl}_5\text{OH}^- + \text{H}_2\text{O}$

<sup>a</sup> To avoid round-off errors, values are calculated and given to four significant figures; their accuracy is difficult to establish but typically will be 1 or 2 orders of magnitude worse than the stated precision.

Vasil'ev and Shorokhova, 1973; Ahrlund and Bovin, 1974). Antimony(III) oxide occurs as two isomorphous forms—orthorhombic  $\text{Sb}_2\text{O}_3(\text{s})$ , existing in nature as the mineral valentinite, and cubic  $\text{Sb}_2\text{O}_3(\text{s})$ , existing as the mineral senarmontite. According to Ahrlund and Bovin (1974), at 25°C, the orthorhombic modification is metastable but the transition into the stable cubic modification does not take place in aqueous solution. As discussed in Pitman et al. (1957), some older studies probably used a mixture of  $\text{Sb}_2\text{O}_3$  crystals that may have been high in the

orthorhombic form (Schuhmann, 1924). Other studies (Gayer and Garrett, 1952; Ahrlund and Bovin, 1974) appear to have characterised the isomorphous form used more satisfactorily. Straightforward comparison of published values is precluded by the different hypotheses made by different authors about the speciation of the soluble antimony species present in equilibrium with the solid phases.

Our data analysis showed that most of the published values for acid-base equilibria and oxides solubilities were neverthe-

Table 4. Best stability constant values for all antimony-sulphide species. Linear combinations of the published reactions used in the calculation of the proposed values are also given.

Reaction	$\log \beta^a$	Linear combination
$2\text{Sb}(\text{OH})_3^0 + 3\text{S}^{2-} + 6\text{H}^+ = 6\text{H}_2\text{O} + \text{Sb}_2\text{S}_3(\text{s})$	91.83	(-) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+3) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$2\text{Sb}(\text{OH})_3^0 + 4\text{S}^{2-} + 7\text{H}^+ = 6\text{H}_2\text{O} + \text{Sb}_2\text{HS}_4^-$	102.4	(+) $\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{Sb}_2\text{HS}_4^-$ (-) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+4) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$2\text{Sb}(\text{OH})_3^0 + 4\text{S}^{2-} + 6\text{H}^+ = 6\text{H}_2\text{O} + \text{Sb}_2\text{S}_4^{2-}$	90.94	(-) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+) $\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{Sb}_2\text{S}_4^{2-} + \text{H}^+$ (+4) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$2\text{Sb}(\text{OH})_3^0 + 4\text{S}^{2-} + 8\text{H}^+ = 6\text{H}_2\text{O} + \text{Sb}_2\text{H}_2\text{S}_4^0$	105.9	(-) $\text{Sb}_2\text{H}_2\text{S}_4^0 = \text{Sb}_2\text{HS}_4^- + \text{H}^+$ (+) $\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{Sb}_2\text{HS}_4^-$ (-) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+4) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$2\text{Sb}(\text{OH})_3^0 + 2\text{S}^{2-} + 4\text{H}^+ = 4\text{H}_2\text{O} + \text{Sb}_2(\text{OH})_2\text{S}_2$	57.67	(+) $\text{Sb}_2\text{S}_3(\text{s}) + 2\text{H}_2\text{O} = \text{Sb}_2(\text{OH})_2\text{S}_2 + \text{H}_2\text{S}$ (-) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (-) $\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}^0$ (+2) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$\text{Sb}(\text{OH})_3^0 + 3\text{S}^{2-} + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbS}_3^0$	46.80	(+) $0.5\text{Sb}_2\text{S}_3(\text{s}) + 1.5\text{S}^{2-} = \text{SbS}_3^0$ (-0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+1.5) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$\text{Sb}(\text{OH})_3^0 + 2\text{S}^{2-} + 3\text{H}^+ = 3\text{H}_2\text{O} + \text{SbS}_2^-$	47.92	(+0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 2\text{HS}^- = 2\text{SbS}_2^- + \text{H}_2\text{S}$ (-0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (-0.5) $\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$ (+2) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$4\text{Sb}(\text{OH})_3^0 + 7\text{S}^{2-} + 12\text{H}^+ = 12\text{H}_2\text{O} + \text{Sb}_4\text{S}_7^{2-}$	183.2	(+) $2\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- + \text{OH}^- = \text{Sb}_4\text{S}_7^{2-} + \text{H}_2\text{O}$ (-2) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+7) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$ (-) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
$\text{Sb}(\text{OH})_3^0 + 4\text{S}^{2-} + 3\text{H}^+ = 3\text{H}_2\text{O} + 2\text{e}^- + \text{SbS}_4^{3-}$	68.20	(+) $2\text{S}^{2-} + \text{SbS}_2^- = \text{SbS}_4^{3-} + 2\text{e}^-$ (+0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 2\text{HS}^- = 2\text{SbS}_2^- + \text{H}_2\text{S}$ (-0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (-0.5) $\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$ (+2) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$
$\text{Sb}(\text{OH})_3^0 + \text{S}^{2-} + \text{H}^+ = \text{H}_2\text{O} + \text{Sb}(\text{OH})_2\text{S}^-$	14.78	(+) $\text{Sb}_2\text{S}_3(\text{s}) + 2\text{OH}^- = 2\text{SbS}_2^- + \text{Sb}(\text{OH})_2\text{S}^-$ (-0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 2\text{HS}^- = 2\text{SbS}_2^- + \text{H}_2\text{S}$ (-0.5) $\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3^0 + 3\text{H}^+ + 3\text{HS}^-$ (+0.5) $\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$ (+) $\text{H}^+ + \text{S}^{2-} = \text{HS}^-$ (-2) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$

<sup>a</sup> To avoid round-off errors, values are calculated and given to four significant figures; their accuracy is difficult to establish but typically will be 1 or 2 orders of magnitude worse than the stated precision.

less thermodynamically consistent, except for all the data of Pavlov and Lazarov (1958a, 1958b) and the data predicted by Pitman et al. (1957) for antimony(V) equilibria. The Pavlov and Lazarov (1958a, 1958b) values are entirely inconsistent

with the others, probably because of some problem with the proposed stoichiometry of the species. In certain cases, extrapolation of values from high ionic strengths to infinite dilution proved difficult and values obtained by linear combination of

other reactions were preferred (i.e., with the reaction  $\text{Sb}_2\text{O}_3(\text{cubic,s}) + \text{H}^+ + 0.5\text{H}_2\text{O} = \text{Sb}(\text{OH})_2^+$ , where the only value published had been determined at 5-mol/L ionic strength).

### 3.3. Chloride

The scarce data on Sb(V)-chloride binding (Neumann, 1954; Neumann and Ramette, 1956; Dakar and Iofa, 1965) have been obtained under extremely acidic conditions, i.e., 6 to 11 mol/L HCl (Neumann, 1954); 9 mol/L HCl (Neumann and Ramette, 1956); 5 to 9 mol/L HCl (Iofa and Dakar, 1965) to prevent hydrolysis. This makes it difficult to establish the strength of such interactions under dilute conditions relative to other antimony species and accordingly no thermodynamic relationship of this kind has been published. The set of species and equilibria included in the database for Sb(V)-chloride could thus not be expressed as a function of the basis species  $\text{Sb}(\text{OH})_3^0$  (see Table 3). It was therefore not possible to calculate the concentrations of these Sb(V)-chloride complexes relative to the concentrations of other Sb species in solution.

Chloroantimonate(III) species in aqueous solution are clearly weak, even though determinations of equilibrium constants for Sb(III)-chloride have been made, often under highly acidic conditions (Pantani and Desideri, 1959; Iofa and Dakar, 1964; Haight and Ellis, 1965; Fridman et al., 1965; Bond and Waugh, 1970; Milne, 1975). A few studies describe relatively more dilute solutions (Iofa and Dakar, 1964; Kondziela and Biernat, 1975). Polarographic methods, which take advantage of Sb(III) being electro-active at the mercury electrode in the presence of chloride ions, have often been exploited (Pantani and Desideri, 1959; Bond and Waugh, 1970; Biernat et al., 1975; Kondziela and Biernat, 1975). However, the data treatment commonly used for polarographic data (DeFord and Hume method, DeFord and Hume, 1951) makes it difficult to establish the maximum stoichiometry of the higher complexes being formed ( $\text{SbCl}_4^-$  vs.  $\text{SbCl}_6^-$ ) with any reasonable degree of confidence. Concomitantly, associated equilibrium constant values become increasingly uncertain as the stoichiometry of the corresponding complexes increases. This may help to explain why all values from Biernat et al. (1975) and Kondziela and Biernat (1975) and values for complexes with stoichiometries >1:2 for Pantani and Desideri (1959) proved unreliable (a weight of zero was assigned to them). Since the remaining constant values had only been obtained at very high ionic strengths, the extrapolation of constant values to infinite dilution proved problematic with most reactions and so the equilibrium constant values

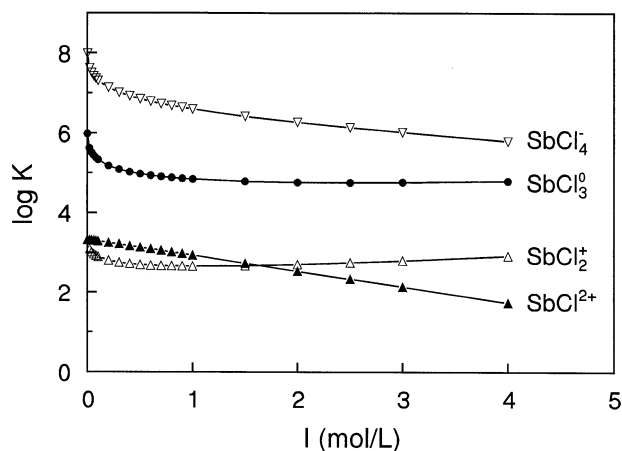


Fig. 1. Plot of the predicted dependence on ionic strength of the formation constants of the different Sb(III)-chloride species. Calculated associated standard deviations are 0.001 for  $\text{SbCl}_2^{2+}$  and  $\text{SbCl}_2^+$  and 0.003 for  $\text{SbCl}_3^0$  and  $\text{SbCl}_4^-$ .

were obtained by linear combination from better established reactions (in the case of the 1:3 and 1:4 complexes). Figure 1 shows the predicted values for conditional stability constants as a function of ionic strength for four Sb(III)-chloride species. The results indicate that  $\text{SbCl}_2^+$  is possibly never formed. The linear nature of the plot for  $\text{SbCl}_2^{2+}$  is due to the particular combination of species charges, which lead to a cancellation of the Debye-Hückel effect (Robinson and Stokes, 1965; Grenthe et al., 1997).

### 3.4. Fluoride

The Sb(III)-fluoride system has been the subject of very few studies (see Appendix, Table A4). One of the studies (Kleiner and Gridchina, 1959) provides a good example of the capability of our JESS-based approach to detect inconsistencies in published data. Table 5 compares the value published for the equilibrium  $\text{Sb}(\text{OH})_2^+ + \text{F}^- = \text{Sb}(\text{OH})_2\text{F}$  with the value obtained automatically for the same reaction by linear combination of other reactions having a higher 'information content', including even one characterized by the same authors. The difference is considerable.

### 3.5. Sulfide

The system antimony-sulfide has been investigated for various conditions relevant to ambient natural waters (Akeret,

Table 5. Example of detection of an inconsistency in published data. Source: Kleiner and Gridchina (1959).

Reaction as published (20°C, 0.1 mol/L $\text{KNO}_3$ ): <sup>a</sup>	$\text{Sb}(\text{OH})_2^+ + \text{F}^- = \text{SbF}(\text{OH})_2$	$\log K = 5.676$
Linear combination:	(+) $\text{Sb}(\text{OH})_3(\text{s}) + \text{HF} = \text{SbF}(\text{OH})_2 + \text{H}_2\text{O}$ (-) $\text{Sb}(\text{OH})_3(\text{s}) = \text{Sb}^{3+} + 3\text{OH}^-$ (+) $\text{H}^+ + \text{F}^- = \text{HF}$ (-) $\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$ (-) $\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb}(\text{OH})_2^+ + \text{H}^+$ (-3) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	$\log K = 1.631$
		$\log K \text{ diff.} = 4.05$

<sup>a</sup> Value extrapolated to 25°C and infinite dilution.



1953; Babko and Lisetskaya, 1956; Dubey and Ghosh, 1962; Arntson et al., 1966; Kolpakova, 1971, 1982; Krupp, 1988; Spycher and Reed, 1989). Due to their presence in geothermal solutions, the nature of antimony sulfide species has also been studied at high temperatures (Krupp, 1988, and references therein). These results have not been included in the present study.

Given the difficulties associated with the characterisation of the species formed, various stoichiometries have been considered (see Appendix, Table A6). Different strategies for establishing reliable equilibrium constants from conflicting and often incomplete experimental measurements, as is the case with this system, are controversial (Spycher and Reed, 1989, 1990; Krupp, 1990). These papers give a comprehensive discussion of the experimental and interpretation limitations encountered. Some points that need to be mentioned here specifically are as follows. First, antimony sulfide can be present as crystalline stibnite or as colloidal or amorphous solids (see Appendix, Table A6), which will certainly have different effective 'solubility products'. Since the non-crystalline solids are more prone to coagulate, measured concentrations in solution may well not represent equilibrium solubilities adequately (Krupp, 1990). However, according to other authors (Spycher and Reed, 1989) the difference in measured solubility between the two phases can be neglected within the limits of the errors involved. Secondly, with the exception of the studies by Akeret (1953) and Kolpakova (1982), as shown in Table A6 of the Appendix, most of the experiments do not cover a significant range of pH. Thirdly, as is unfortunately so often the case, the ionic strength has not been held constant in any of the solubility measurements.

Our analysis showed that the existing data were for the most part consistent thermodynamically. An exception is the value given by Akeret (1953) for the reaction  $0.5\text{Sb}_2\text{S}_3(\text{s}) + 3\text{H}^+ + 4\text{Cl}^- = \text{SbCl}_4^- + 1.5\text{H}_2\text{S}$ , presumably because of the value used by the author for the formation of  $\text{SbCl}_4^-$ . All the values published by Krupp (1988) extrapolated to infinite dilution appear to be systematically inconsistent with values obtained by linear combination from other reactions. This was also the case for the values given by Dubey and Ghosh (1962) for reaction  $\text{Sb}_2\text{S}_3(\text{s}) + \text{S}^{2-} = \text{Sb}_2\text{S}_4^{2-}$  and by Babko and Lisetskaya (1956) for reaction  $0.5\text{Sb}_2\text{S}_3(\text{s}) + 0.5\text{S}^{2-} = \text{SbS}_2^-$ , respectively.

### 3.6. Speciation Calculations

Once the 'best' set of reactions and equilibrium constant values had been determined, speciation calculations were performed under conditions typical for (1) freshwater oxic waters (typical composition as given in Stumm and Morgan, 1996); (2) seawater surface waters (composition as given in Whitfield and Jagner, 1981); (3) sulfide-free anoxic freshwaters; and (4) sulfide-rich freshwaters (total antimony and sulfide concentrations as measured in sediments of freshwater lakes, Chen et al., submitted). The results obtained show that antimony is exclusively present as  $\text{Sb}(\text{OH})_6^-$  in oxic systems and as  $\text{Sb}(\text{OH})_3^0$  in anoxic conditions, at all pH values of environmental relevance for aquatic systems.

No formation of Sb(III)-chloride species is observed under seawater conditions; the concentration of possible Sb(V)-chloro-

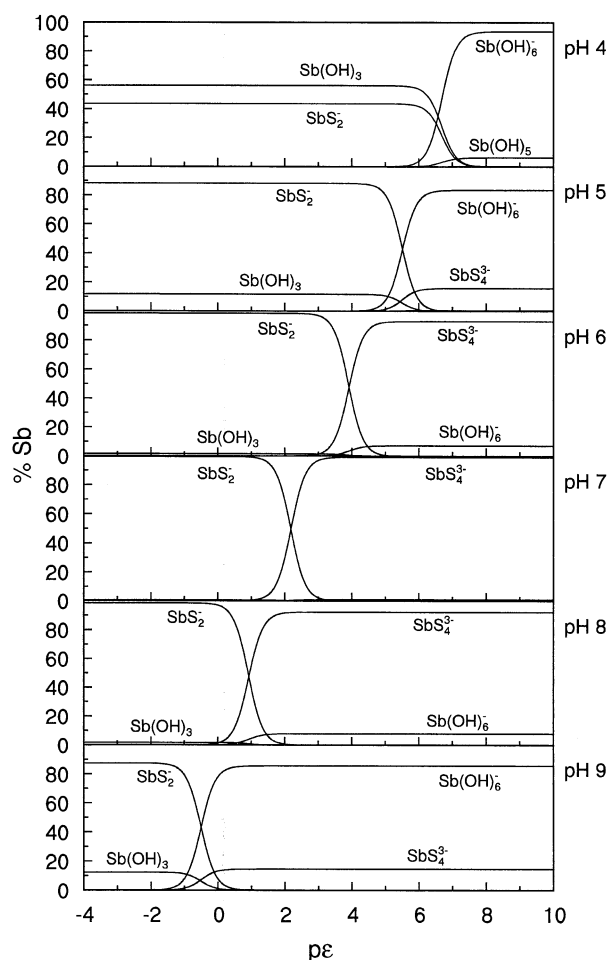


Fig. 2. Antimony-sulfide species distribution as a function of the redox conditions for different pH values. Antimony ( $1.10^{-9}$  mol/L) and sulfide ( $1.10^{-6}$  mol/L) concentrations used are representative of those measured in natural freshwater and sediment systems (Chen et al., 2003). Note that this calculation assumes that the system is in a 'quasi-equilibrium' where the oxidation of sulfide is kinetically precluded.

ride species could not be calculated, as discussed above. Antimony speciation in sulfide-rich waters is dominated by the formation of soluble sulfide-containing species. When sulfide is present under relatively oxic conditions (Benoit et al., 1997), the predominant formation of  $\text{SbS}_4^{3-}$  is predicted at some pH values. Recently, the formation of Sb(V) thioanions by dissolution of stibnite in deoxygenated aqueous NaHS solutions was confirmed by X-ray absorption spectroscopy (Mosselmans et al., 2000) and the presence of Sb(V) in sulfide-containing waters has been reported (Bertine and Lee, 1983; Cutter, 1991; Chen et al., submitted). Figure 2 illustrates the complexity of Sb speciation just in the presence of sulfide in natural systems. Note that this calculation assumes that the system is in a 'quasi-equilibrium' where the oxidation of sulfide is kinetically precluded. This is a commonly observed scenario, in which Sb(V) and sulfide can co-exist for a significant period even under oxic conditions (Bertine and Lee, 1983; Cutter, 1991; Chen et al., submitted), allowing formation of the species  $\text{SbS}_4^{3-}$ . In practice, a wide variety of antimony species may in

fact occur in the same system because of such 'quasi-equilibria' and because of the frequent occurrence in natural waters of numerous intermediate zones with pH and redox conditions differing from those of the bulk.

#### 4. DISCUSSION

Many, and sometimes arbitrary, decisions have been taken during the development of the current speciation models. This is always the case with equilibrium simulations of multicomponent electrolyte solutions involving many possible chemical species—the thermodynamic data used are derived from many sources that are naturally incoherent and of varying quality. In establishing a thermodynamically consistent set of mass balance equations, choices between differing values must be made and appropriate methods of extrapolation devised to cover modelling conditions outside the range of available experimental measurements. The value of all non-trivial chemical speciation models depends on how well these decisions are made.

Typically, the detail of the decision-making process underlying chemical speciation models is lost. This problem includes inadequate metrological 'traceability' (Meinrath, 2000) but goes well beyond it. In particular, many choices are typically involved which, had they been made differently, would likely lead to different outcomes. For example, there is the omission of outliers (something which is generally necessary but not often comprehensively recorded). Unfortunately, with thermodynamic data, such 'outliers' quite often represent the correction of some systematic experimental error in the earlier, frequently cited studies. Distinguishing between experimentally aberrant data and a singular methodologic advance is therefore a matter of judgement, not statistics.

Since it is unlikely that the enormous number of decisions involved in the development of complicated thermodynamic models can always be made correctly, much greater attention should be given to the decision-making procedures themselves. In particular, this requires that the process followed be systematic and reproducible. It is now clear that for all but the most trivial of chemical speciation models this is not possible without computer automation. Indeed, it seems that without such automation, the complexity of thermodynamic calculations becomes a formidable obstacle to progress, especially with ionic systems like those that occur in aquatic chemistry (because of their non-ideal behaviour). This problem is often confused with the issue of describing the non-ideal behaviour theoretically (as activity coefficients). In fact, the latter is generally much less problematic than the consequences for chemical speciation models of poor numerical methods, incorrect assessment of data, error propagation and (consequently) wayward extrapolations.

Of key importance therefore is that the various decisions made during the process of model development are recorded so that subsequently alternatives can be readily tested. In this way, the model can be progressively improved both by the appearance of new data and by the identification and correction of bad judgements. The hope is that this will eventually achieve a convergence of modelling outcomes that has hitherto been so often noticeably lacking.

In this work, we have developed a model for antimony in natural waters. This is an element of increasing environmental

significance but one whose chemical speciation has not previously been modelled in any comprehensive way. It therefore provides a good test of the computer methodology that is emerging. It will be interesting to see how the results of the present modelling compare with future developments.

Finally, it is noteworthy that antimony in natural waters is found mostly in the dissolved phase (Filella et al., 2002b) so the present calculated l.m.w. speciation can be considered to account reasonably for the actual behaviour of antimony in the aquatic systems. On the other hand, the observed oxidation states (Filella et al., 2002a) are less well predicted by these thermodynamic models, emphasising the important role of kinetics in the environmental cycling of this element.

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## APPENDIX

Table A1. List of abbreviations.

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EFEF:	estimated from free energies of formation
KIN:	measured, kinetic method
MDS:	measured, distribution between two phases
MEF:	measured, electromotive force
MPL:	measured, polarography
MSL:	measured, solubility
MSP:	measured, spectroscopy

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Table A2. Published antimony redox potentials.

Reaction <sup>a</sup>	<i>E</i> (V)	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Technique	Reference
$\text{Sb(s)} + 3\text{S}^{2-} = \text{SbS}_3^{3-} + 3\text{e}^-$	-0.830	25	Infinite dilution	MEF	Chazov (1976)
$4\text{Sb(s)} + 12\text{OH}^- = \text{Sb}_4\text{O}_6(\text{s}) + 6\text{H}_2\text{O} + 12\text{e}^-$	-0.6831	25	Infinite dilution	MEF	Vasilev et al. (1973)
$\text{Sb(s)} + 4\text{OH}^- = \text{SbO}_2^- + 2\text{H}_2\text{O} + 3\text{e}^-$	0.6389 <sup>b</sup>				
$\text{Sb}_4\text{O}_6(\text{s}) + 12\text{H}^+ + 12\text{e}^- = 4\text{Sb(s)} + 6\text{H}_2\text{O}$	0.1545 <sup>b</sup>	15	Infinite dilution	MEF	Vasilev and Shorokhova (1972)
	0.1504 <sup>b</sup>	25			
	0.1468 <sup>b</sup>	35			
	0.1391 <sup>b</sup>	50			
$\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- = \text{Sb(s)} + \text{H}_2\text{O}$	0.2105 <sup>b</sup>	15			
	0.2040 <sup>b</sup>	25			
	0.2003 <sup>b</sup>	35			
	0.1988 <sup>b</sup>	50			
$\text{Sb}_2\text{O}_5(\text{s}) + 4\text{H}^+ + 4\text{e}^- = \text{Sb}_2\text{O}_3(\text{s}) + 2\text{H}_2\text{O}$		25	Infinite dilution	EFEF	Pitman et al. (1957)
Valentinite (orthorhombic form of $\text{Sb}_2\text{O}_3(\text{s})$ )	0.649 <sup>c</sup>				
Senarmontite (cubic form of $\text{Sb}_2\text{O}_3(\text{s})$ )	0.671 <sup>c</sup>				
$\text{Sb}_2\text{O}_3(\text{s}) + 2\text{H}_2\text{O} = \text{Sb}_2\text{O}_5(\text{s}) + 4\text{H}^+ + 4\text{e}^-$	-0.692 <sup>d,e</sup>	25	Infinite dilution	EFEF	Latimer (1952)
$2\text{SbO}^+ + 3\text{H}_2\text{O} = \text{Sb}_2\text{O}_5(\text{s}) + 6\text{H}^+ + 4\text{e}^-$	-0.581 <sup>c</sup>				
$\text{SbO}_2^- + 5\text{OH}^- = \text{H}_3\text{SbO}_6^{4-} + \text{H}_2\text{O} + 2\text{e}^-$	≈0.40 <sup>f</sup>				
$\text{Sb(s)} + 4\text{OH}^- = \text{SbO}_2^- + 2\text{H}_2\text{O} + 3\text{e}^-$	0.66 <sup>c</sup>				
$\text{Sb(s)} + 3\text{H}^+ + 3\text{e}^- = \text{SbH}_3(\text{g})$	-0.51 <sup>c,d,e</sup>				
$\text{Sb(s)} + 2\text{S}^{2-} = \text{SbS}^{2-} + 3\text{e}^-$	0.85				
$2\text{S}^{2-} + \text{SbS}_2^- = \text{SbS}_3^{3-} + 2\text{e}^-$	≈0.6				
$\text{Sb(V)} + 2\text{e}^- = \text{Sb(III)}$	0.818 <sup>d</sup>	25	6.0 HCl	MEF	Brown and Swift (1949)
	0.784 <sup>d</sup>		4.5 HCl		
	0.746 <sup>d,e</sup>		3.5 HCl		
$\text{Sb(s)} + 1.5\text{H}_2\text{O} = 0.5\text{Sb}_2\text{O}_3(\text{s}) + 3\text{H}^+ + 3\text{e}^-$	-0.152 <sup>g</sup>	25	0.2–1.1 $\text{HClO}_4$	MEF	Schuhmann (1924)
$\text{Sb(s)} + \text{H}_2\text{O} = \text{SbO}^+ + 2\text{H}^+ + 3\text{e}^-$	-0.212 <sup>g</sup>				
$\text{SbO}_2^- + 2\text{OH}^- = \text{SbO}_3^- + \text{H}_2\text{O} + 2\text{e}^-$	-0.589 <sup>d,h,i</sup>	20	10.0 KOH	MEF	Grube and Schweigardt (1923)
	-0.578		9 KOH		
	-0.568		8 KOH		
	-0.561 <sup>d</sup>		7.5 KOH		
	-0.554		7 KOH		
	-0.539		6 KOH		
	-0.516 <sup>d</sup>		5 KOH		
	-0.484		4 KOH		
	-0.428 <sup>d</sup>		3 KOH		
$\text{Sb(s)} + 4\text{OH}^- = \text{SbO}_2^- + 2\text{H}_2\text{O} + 3\text{e}^-$	0.675 <sup>d</sup>		10.0 KOH		

<sup>a</sup> Compounds have been written in the form used by the authors. Correspondences:  $\text{HSbO}_3 \approx \text{H}[\text{Sb}(\text{OH})_6] \approx \text{Sb}(\text{OH})_5$ ;  $\text{SbO}_2^+ \approx \text{Sb}(\text{OH})_4^+$ ;  $\text{SbO}_3^- \approx \text{Sb}(\text{OH})_6^-$ ;  $\text{HSbO}_2 \approx \text{H}_3\text{SbO}_3 \approx \text{Sb}(\text{OH})_3 \approx \text{SbO}(\text{OH})$ ;  $\text{SbO}^+ \approx \text{Sb}(\text{OH})_2^+$ ;  $\text{SbO}_2^- \approx \text{Sb}(\text{OH})_4^-$ .

<sup>b</sup> Value reproduced in Hogfeldt (1982).

<sup>c</sup> Value reproduced in Lide and Frederikse (1995).

<sup>d</sup> Value reproduced in Sillen and Martell (1964).

<sup>e</sup> Value reproduced in Kotrly and Sucha (1985).

<sup>f</sup> According to Latimer (1952), there is no evidence that Sb(V) is present as  $\text{SbO}_3^-$  (as suggested by Grube and Schweigardt, 1923). If it is present as  $\text{H}_3\text{SbO}_6^{4-}$ , Latimer proposes a potential around 400 mV for this equilibrium.

<sup>g</sup> Values given in Sillen and Martell (1964) as being valid at infinite dilution.

<sup>h</sup> Value reproduced in Kotrly and Sucha (1985). Temperature is wrongly quoted.

<sup>i</sup> Value reproduced in Lide and Frederikse (1995). Ionic strength and temperature are wrongly quoted.

Table A3. Published antimony acid-base and oxide solubility constants.

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Technique	Reference
$\text{Sb}^{3+} + \text{OH}^- = \text{SbOH}^{2+}$	14.61	25	1.0 (H,Na)ClO <sub>4</sub>	MSP (gallein)	Antonovich et al. (1977)
$\text{Sb}^{3+} + 2\text{OH}^- = \text{Sb(OH)}_2^+$	28.62				
$\text{Sb}^{3+} + 3\text{OH}^- = \text{Sb(OH)}_3^0$	41.57				
$\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbOH}^{2+} + \text{H}^+$	0.61				
$\text{SbOH}^{2+} + \text{H}_2\text{O} = \text{Sb(OH)}_2^+ + \text{H}^+$	0.013				
$\text{Sb(OH)}_2^+ + \text{H}_2\text{O} = \text{Sb(OH)}_3^0 + \text{H}^+$	-1.05				
$\text{Sb(OH)}_3^0 + \text{H}^+ = \text{Sb(OH)}_2^+ + \text{H}_2\text{O}$	1.41	25	Infinite dilution	Data reinterpretation, based on Gayer and Garrett (1952)	Baes and Mesmer (1976)
$\text{Sb(OH)}_3^0 + \text{H}_2\text{O} = \text{Sb(OH)}_4^- + \text{H}^+$	-11.82				
$0.5\text{Sb}_2\text{O}_3(\text{s}) + 1.5\text{H}_2\text{O} = \text{Sb(OH)}_3^0$	-4.24				
$0.5\text{Sb}_2\text{O}_5(\text{s}) + 2.5\text{H}_2\text{O} = \text{Sb(OH)}_5^0$	-3.7 <sup>b</sup>	35	0.05–4.6 HCl	Calculated from Tourky and Mousa (1948) solubility data	Baes and Mesmer (1976)
$\text{Sb(OH)}_5^0 + \text{H}_2\text{O} = \text{Sb(OH)}_6^- + \text{H}^+$	-2.72 <sup>c</sup>	25	Infinite dilution	Recalculated from Lefebvre and Maria (1963)	Baes and Mesmer (1976)
$12\text{Sb(OH)}_5^0 + 4\text{H}_2\text{O} = \text{Sb}_{12}(\text{OH})_{64}^{4-} + 4\text{H}^+$	20.34				
$12\text{Sb(OH)}_5^0 + 5\text{H}_2\text{O} = \text{Sb}_{12}(\text{OH})_{65}^{5-} + 5\text{H}^+$	16.72				
$12\text{Sb(OH)}_5^0 + 6\text{H}_2\text{O} = \text{Sb}_{12}(\text{OH})_{66}^{6-} + 6\text{H}^+$	11.89				
$12\text{Sb(OH)}_5^0 + 7\text{H}_2\text{O} = \text{Sb}_{12}(\text{OH})_{67}^{7-} + 7\text{H}^+$	6.07				
$\text{Sb(OH)}_3^0 + \text{H}^+ = \text{Sb(OH)}_2^+ + \text{H}_2\text{O}$	1.23 <sup>d,e</sup>	25	3.0 NaClO <sub>4</sub>	MDS + radiotracers	Shoji et al. (1974)
$0.5\text{Sb}_2\text{O}_3(\text{s}) + \text{H}^+ = \text{Sb(OH)}_2^+ + 0.5\text{H}_2\text{O}$		25	5.0 (H,Na)ClO <sub>4</sub>	MSL	Ahrland and Bovin (1974)
Orthorhombic Sb <sub>2</sub> O <sub>3</sub> (s)	-3.06 <sup>f,g,h</sup>				
Cubic Sb <sub>2</sub> O <sub>3</sub> (s)	-3.18 <sup>f,g,h</sup>				
$2\text{Sb(OH)}_2^+ + 2\text{H}^+ = \text{Sb}_2(\text{OH})_4^{4+} + 2\text{H}_2\text{O}$	0.68 <sup>f,g</sup>				
$\text{Sb(OH)}_2^+ + \text{H}^+ = \text{SbOH}^{2+} + \text{H}_2\text{O}$	-0.86 <sup>i</sup>				
$\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4(\text{H}_2\text{O})_{1/2}(\text{s}) + 3\text{H}^+ + 3/2\text{H}_2\text{O} = 4\text{Sb}_2(\text{OH})_2^{4+} + \text{ClO}_4^-$	-13.07 <sup>e</sup>				
$\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2(\text{s}) + 2\text{H}^+ + 2\text{H}_2\text{O} = 4\text{Sb}_2(\text{OH})_2^{4+} + 2\text{NO}_3^-$	-13.46 <sup>e</sup>		5.0 (H,Na)NO <sub>3</sub>		
$\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2(\text{s}) + 6\text{H}^+ = 4\text{SbOH}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$	-16.89 <sup>c</sup>				
$1/4\text{Sb}_4\text{O}_6(\text{s}) + 3/2\text{H}_2\text{O} + \text{OH}^- = \text{Sb(OH)}_4^-$	-2.44 <sup>e</sup> -2.35 <sup>e</sup> -2.21 <sup>e</sup> -2.08 <sup>e</sup> -2.22 <sup>e</sup>	15 25 35 50 25	Infinite dilution   2 NaClO <sub>4</sub>	MSL	Vasil'ev and Shorokhova (1973)
$\text{H}_3\text{SbO}_3 + \text{H}^+ = \text{SbO}^+ + 2\text{H}_2\text{O}$	1.42 <sup>j</sup>	23	Variable (≤0.1) HClO <sub>4</sub>	MSP	Mishra and Gupta (1968)
$0.5\text{Sb}_2\text{O}_3(\text{s}) + \text{H}^+ = \text{SbO}^+ + 0.5\text{H}_2\text{O}$	-3.1	25	0.2–1.1 HClO <sub>4</sub>	MSL	Fridman et al. (1965)
$\text{Sb(OH)}_6^- + \text{H}^+ = \text{HSb(OH)}_6$	-2.55	25	0.5 (CH <sub>3</sub> ) <sub>4</sub> NCl		Lefebvre and Maria (1963)

Table A3. continued

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Technique	Reference
$\text{Sb}_{12}\text{H}_4^{8-} + \text{H}^+ = \text{Sb}_{12}\text{H}_5^{7-}$	-7.15				
$\text{Sb}_{12}\text{H}_5^{7-} + \text{H}^+ = \text{Sb}_{12}\text{H}_6^{6-}$	-5.75				
$\text{Sb}_{12}\text{H}_6^{6-} + \text{H}^+ = \text{Sb}_{12}\text{H}_7^{5-}$	-4.35				
$\text{Sb}_{12}\text{H}_7^{5-} + \text{H}^+ = \text{Sb}_{12}\text{H}_8^{4-}$	-2.95				
$\text{Sb}_{12}\text{H}_8^{4-} + \text{H}^+ = \text{Sb}_{12}\text{H}_9^{3-}$	-1.55				
$12\text{Sb}(\text{OH})_6^- + 4\text{H}^+ = \text{H}_4\text{Sb}_{12}^{8-}$	-33.3				
$\text{Sb}(\text{OH})_3(\text{s}) = \text{Sb}^{3+} + 3\text{OH}^-$	-41.5 <sup>k</sup>	12	0.01–0.02 HCl	MPL	Kovalenko (1958)
$\text{Sb}(\text{OH})_3^0 = \text{Sb}^{3+} + 3\text{OH}^-$	-43.6	25	0.5 KCl	MPL	Pavlov and Lazarov (1958a, 1958b)
$\text{Sb}(\text{OH})_2^+ = \text{Sb}^{3+} + 2\text{OH}^-$	-47				
$\text{Sb}(\text{OH})^{2+} = \text{Sb}^{3+} + \text{OH}^-$	-46				
$\text{HSbO}_2^0 + \text{H}^+ = \text{SbO}^+ + \text{H}_2\text{O}$	0.87 <sup>k</sup>	25	Infinite dilution	EFEF	Pitman et al. (1957)
$\text{Sb}(\text{OH})_4^- + \text{H}^+ = \text{HSbO}_2^0 + 2\text{H}_2\text{O}$	11.0 <sup>k</sup>				
$\text{Sb}(\text{OH})_6^- + 2\text{H}^+ = \text{SbO}_2^+ + 4\text{H}_2\text{O}$	0.54				
$\text{Sb}_2\text{O}_5(\text{s}) + 2\text{H}^+ = 2\text{SbO}_2^+ + \text{H}_2\text{O}$	-4.70				
$2\text{Sb}(\text{OH})_6^- + 2\text{H}^+ = \text{Sb}_2\text{O}_5 + 7\text{H}_2\text{O}$	-4.16				
$0.5\text{Sb}_2\text{O}_3(\text{s}) + \text{H}^+ = \text{SbO}^+ + 0.5\text{H}_2\text{O}$	-3.11 <sup>l,m</sup>	25	0–0.1 HCl	MSL	Gayer and Garrett (1952)
$0.5\text{Sb}_2\text{O}_3(\text{s}) + 1.5\text{H}_2\text{O} = \text{Sb}(\text{OH})_3^0$	-4.24 <sup>n</sup>		Infinite dilution		
$0.5\text{Sb}_2\text{O}_3(\text{s}) + \text{OH}^- = \text{SbO}_2^- + 1.5\text{H}_2\text{O}$ (rhombic $\text{Sb}_2\text{O}_3$ )	-2.06 <sup>k</sup>		0–0.1 NaOH		
$\text{Sb}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Sb}(\text{OH})_3^0 + \text{H}^+$	-1.4 <sup>k</sup>	25	Infinite dilution	MSL	Kasper (1941)
$\text{Sb}(\text{OH})_4^- + \text{H}^+ = \text{Sb}(\text{OH})_3^0 + \text{H}_2\text{O}$	11.8 <sup>k</sup>				
$\text{Sb}(\text{OH})_3(\text{s}) = \text{Sb}^{3+} + 3\text{OH}^-$	-41.4 <sup>k</sup>	Not given	Variable	MPL	Bayerle (1925)
$0.5\text{Sb}_2\text{O}_3(\text{s}) + \text{H}^+ = \text{SbO}^+ + 0.5\text{H}_2\text{O}$	-3.1 <sup>k</sup>	25	0.2–1.1 $\text{HClO}_4$	MSL	Schuhmann (1924)

<sup>a</sup> Compounds have been written in the form used by the authors. Correspondances:  $\text{HSbO}_3 \approx \text{H}[\text{Sb}(\text{OH})_6] \approx \text{Sb}(\text{OH})_5$ ;  $\text{SbO}_2^+ \approx \text{Sb}(\text{OH})_4^+$ ;  $\text{SbO}_3^- \approx \text{Sb}(\text{OH})_6^-$ ,  $\text{HSbO}_2 \approx \text{H}_3\text{SbO}_3 \approx \text{Sb}(\text{OH})_3 \approx \text{SbO}(\text{OH})$ ;  $\text{SbO}^+ \approx \text{Sb}(\text{OH})_2^+$ ;  $\text{SbO}_2^- \approx \text{Sb}(\text{OH})_4^-$ .

<sup>b</sup> According to Baes and Mesmer (1976), it is not likely that a pure solid phase was present.

<sup>c</sup> Value reproduced by Kotrly and Sucha (1985).

<sup>d</sup> Value probably used by Martell et al. (1993) to calculate log *K* = 13.0 recommended for the reaction  $\text{Sb}(\text{OH})_2^- + \text{OH}^- = \text{Sb}(\text{OH})_3$  (25°C, *I* = 3 mol/L, no background electrolyte given).

<sup>e</sup> Value reproduced in Hogfeldt (1982).

<sup>f</sup> Value recommended by Martell et al. (1993). Background electrolyte not given.

<sup>g</sup> Values used by Hogfeldt (1982) to calculate the following constant values (25°C, *I* = 5 mol/L  $\text{NaClO}_4$ ):  $\text{Sb}_4\text{O}_6(\text{s, cubic}) + 4\text{H}^+ + 2\text{H}_2\text{O} = 4\text{Sb}(\text{OH})_2^+$ , log *K* = -12.7;  $\text{Sb}_4\text{O}_6(\text{s, rhombic}) + 4\text{H}^+ + 2\text{H}_2\text{O} = 4\text{Sb}(\text{OH})_2^+$ , log *K* = -12.2;  $\text{Sb}_4\text{O}_6(\text{s, cubic}) + 8\text{H}^+ = 2\text{Sb}_2(\text{OH})_4^{2+} + 2\text{H}_2\text{O}$ , log *K* = -11.71;  $\text{Sb}_4\text{O}_6(\text{s, rhombic}) + 8\text{H}^+ = 2\text{Sb}_2(\text{OH})_4^{2+} + 2\text{H}_2\text{O}$ , log *K* = -10.86.

<sup>h</sup> Values used by Kotrly and Sucha (1985) to calculate the following constant values (25°C, *I* = 5 mol/L, no background electrolyte given):  $0.5\text{Sb}_2\text{O}_3(\text{s, cubic}) + 1.5\text{H}_2\text{O} = \text{Sb}(\text{OH})_2^+ + \text{OH}^-$ , log *K* = -17.78;  $0.5\text{Sb}_2\text{O}_3(\text{s, cubic}) + 1.5\text{H}_2\text{O} = \text{Sb}(\text{OH})_2^+ + \text{OH}^-$ , log *K* = -17.66.

<sup>i</sup> Value probably used by Martell et al. (1993) to calculate log *K* = 15.5 for reaction  $\text{SbOH}^{2+} + \text{OH}^- = (\text{SbOH})_2^+$  (25°C, *I* = 5 mol/L, no background electrolyte given).

<sup>j</sup> Value reproduced in Sillén and Martell (1971).

<sup>k</sup> Value reproduced in Sillén and Martell (1964).

<sup>l</sup> Value reproduced in Sillén and Martell (1964) as -3.11 at infinite dilution.

<sup>m</sup> Value reproduced in Martell et al. (1993) as -3.09 at infinite dilution.

<sup>n</sup> Value reproduced in Sillén and Martell (1964) as -4.70 at infinite dilution.

Table A4. Published antimony-chloride stability constants.

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Acidity	Technique	Reference
$\text{Sb}^{3+} + \text{Cl}^- = \text{SbCl}_2^+$	0.96	22	4.0 (H,Na)ClO <sub>4</sub> ([Cl <sup>-</sup> ] = 0–4 mol/L)	0.5 mol/L HClO <sub>4</sub>	MPL	Biernat et al. (1975)
$\text{Sb}^{3+} + 2 \text{Cl}^- = \text{SbCl}_2^+$	1.52					
$\text{Sb}^{3+} + 3 \text{Cl}^- = \text{SbCl}_3^0$	1.45					
$\text{Sb}^{3+} + 4 \text{Cl}^- = \text{SbCl}_4^-$	1.04					
$\text{Sb}^{3+} + 2 \text{Cl}^- = \text{SbCl}_2^+$	3.39			4.0 mol/L HClO <sub>4</sub>		
$\text{Sb}^{3+} + 3 \text{Cl}^- = \text{SbCl}_3^0$	4.09					
$\text{Sb}^{3+} + \text{Cl}^- = \text{SbCl}_2^+$	1.05	20	4.70 (H,Na)ClO <sub>4</sub> ([Cl <sup>-</sup> ] = 0.1 mol/L)	0.7 mol/L HClO <sub>4</sub>	MPL	Kondziela and Biernat (1975)
$\text{Sb}^{3+} + 2 \text{Cl}^- = \text{SbCl}_2^+$	1.90					
$\text{Sb}^{3+} + 3 \text{Cl}^- = \text{SbCl}_3^0$	2.20					
$\text{Sb}^{3+} + 4 \text{Cl}^- = \text{SbCl}_4^-$	1.95					
$\text{Sb}^{3+} + 5 \text{Cl}^- = \text{SbCl}_5^{2-}$	1.10					
$\text{SbCl}_4^- + 2 \text{Cl}^- = \text{SbCl}_6^{3-}$	-0.74	25	3–12 HCl	3–12 mol/L HCl	MSP	Milne (1975)
$\text{Sb}^{3+} + \text{Cl}^- = \text{SbCl}_2^+$	2.3 <sup>b,c</sup>	30	5.0 HClO <sub>4</sub> ([Cl <sup>-</sup> ] = 0–0.77 mol/L)	5.0 mol/L HClO <sub>4</sub>	MPL	Bond and Waugh (1970)
$\text{Sb}^{3+} + 2 \text{Cl}^- = \text{SbCl}_2^+$	4.0 <sup>b,c</sup> , 4.2 <sup>b</sup>					
$\text{Sb}^{3+} + 3 \text{Cl}^- = \text{SbCl}_3^0$	5.8 <sup>b,c</sup> , 6.0 <sup>b</sup>					
$\text{Sb}^{3+} + 4 \text{Cl}^- = \text{SbCl}_4^-$	6.8 <sup>b,c</sup> , 7.1 <sup>b</sup>					
$\text{SbOCl}(s) + \text{H}^+ + 2 \text{Cl}^- = \text{SbOHCl}_3^-$	-1.2	25	6.0 (H,Na)ClO <sub>4</sub>	1–4 mol/L HClO <sub>4</sub>	MSL + MSP	Fridman et al. (1965)
$\text{SbOHCl}_3^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_4^- + \text{H}_2\text{O}$	0.18					
$\text{SbCl}_3^0 + \text{Cl}^- = \text{SbCl}_4^-$	1.0 <sup>d</sup>	25	4.0 H <sub>2</sub> SO <sub>4</sub>	4.0 mol/L H <sub>2</sub> SO <sub>4</sub>	MSL	Haight and Ellis (1965)
$\text{SbCl}_4^- + 2 \text{Cl}^- = \text{SbCl}_6^{3-}$	-0.77 <sup>d</sup>					
$\text{SbCl}_3(\text{OH})_3^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_4(\text{OH})_2^- + \text{H}_2\text{O}$	-3.07 <sup>d</sup>	?	Infinite dilution		MDS	Dakar and Iofa (1965)
$\text{SbCl}_4(\text{OH})_2^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_5(\text{OH})^- + \text{H}_2\text{O}$	-3.46 <sup>d</sup>					
$\text{SbCl}_5(\text{OH})^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_6^- + \text{H}_2\text{O}$	-4.28 <sup>d</sup>					
$\text{SbCl}_3^0 + \text{Cl}^- = \text{SbCl}_4^-$	1.3 <sup>d</sup> to 1.5 <sup>d</sup>	15	6.3 Li(Cl,NO <sub>3</sub> )	0.5 mol/L HCl	MDS	Iofa and Dakar (1964) <sup>e</sup>
$\text{SbCl}_4^- + 2 \text{Cl}^- = \text{SbCl}_6^{3-}$	-1.1 <sup>d</sup> to -0.8 <sup>d</sup>					
$\text{Sb}^{3+} + \text{Cl}^- = \text{SbCl}_2^+$	2.26 <sup>f</sup>	25	4.0 HClO <sub>4</sub>	4.0 mol/L HClO <sub>4</sub>	MPL	Pantani and Desideri (1959)
$\text{Sb}^{3+} + 2 \text{Cl}^- = \text{SbCl}_2^+$	3.49 <sup>f</sup>					
$\text{Sb}^{3+} + 3 \text{Cl}^- = \text{SbCl}_3^0$	4.18 <sup>f</sup>					
$\text{Sb}^{3+} + 4 \text{Cl}^- = \text{SbCl}_4^-$	4.72 <sup>f</sup>					
$\text{Sb}^{3+} + 5 \text{Cl}^- = \text{SbCl}_5^{2-}$	4.72 <sup>f</sup>					
$\text{Sb}^{3+} + 6 \text{Cl}^- = \text{SbCl}_6^{3-}$	4.11 <sup>f</sup>					



Table A4. continued

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Acidity	Technique	Reference
$\text{SbCl}_3\text{OH}^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_6^- + \text{H}_2\text{O}$	-4.3	25	9 (H,Li)Cl	0.01–9 mol/L HCl	KIN	Neumann and Ramette (1956)
$\text{SbCl}_4(\text{OH})_2^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_5\text{OH}^- + \text{H}_2\text{O}$	-3.43	25.6	6–9 HCl	6–9 mol/L HCl	MSP	Neumann (1954)
$\text{SbCl}_5\text{OH}^- + \text{H}^+ + \text{Cl}^- = \text{SbCl}_6^- + \text{H}_2\text{O}$	-4.65		8–11 HCl	8–11 mol/L HCl		
$\text{SbCl}_3(\text{s}) + \text{H}_2\text{O} = \text{SbO}^+ + 2\text{H}^+ + 3\text{Cl}^-$	$\Delta G = -1.5 \text{ kcal}$	25	Infinite dilution		EFEF	Latimer (1952)

<sup>a</sup> Compounds have been written in the form used by the authors. Correspondences:  $\text{HSbO}_3 \approx \text{H}[\text{Sb}(\text{OH})_6] \approx \text{Sb}(\text{OH})_5$ ;  $\text{SbO}_2^+ \approx \text{Sb}(\text{OH})_4^+$ ;  $\text{SbO}_3^- \approx \text{Sb}(\text{OH})_6^-$ ;  $\text{HSbO}_2 \approx \text{H}_3\text{SbO}_3 \approx \text{Sb}(\text{OH})_3 \approx \text{SbO}(\text{OH})$ ;  $\text{SbO}^+ \approx \text{Sb}(\text{OH})_2^+$ ;  $\text{SbO}_2^- \approx \text{Sb}(\text{OH})_4^-$ .

<sup>b</sup> Value reproduced in Hogfeldt (1982). Ionic strength and inert electrolyte are wrongly quoted.

<sup>c</sup> Value recommended in Martell et al. (1993). Background electrolyte not given.

<sup>d</sup> Value reproduced in Sillén and Martell (1971).

<sup>e</sup> Values in a previous publication of the same authors (Iofa and Dakar, 1963) have not been retained because of the uncertainty in the stoichiometry of the reactions quoted.

<sup>f</sup> Value reproduced in Sillén and Martell (1964).

Table A5. Published antimony-fluoride stability constants.

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	<i>I</i> (mol/L) electrolyte	Acidity	Technique	Reference
$\text{Sb}^{3+} + \text{F}^- = \text{SbF}^+$	3.0 <sup>b,c,e</sup>	30	2.0 (H,Na)ClO <sub>4</sub>	1.2 mol/L HClO <sub>4</sub>	MPL	Bond (1970)
$\text{Sb}^{3+} + 2 \text{F}^- = \text{SbF}_2^+$	5.7 <sup>b,d,e</sup>					
$\text{Sb}^{3+} + 3 \text{F}^- = \text{SbF}_3^+$	8.3 <sup>b,d,e</sup>					
$\text{Sb}^{3+} + 4 \text{F}^- = \text{SbF}_4^+$	10.9 <sup>b,d,e</sup>					
$\text{Sb}(\text{OH})_2^+ + \text{F}^- = \text{Sb}(\text{OH})_2\text{F}$	5.5	20	0.10 HNO <sub>3</sub>	pH = 1	MSL	Kleiner and Gridchina (1959)
$\text{Sb}(\text{OH})_3(\text{s}) + \text{HF} = \text{Sb}(\text{OH})_2\text{F} + \text{H}_2\text{O}$	-0.37					
$\text{SbF}_6 = \text{Sb}^{3+} + 6 \text{F}^-$	-36 <sup>f</sup>	25	0.5 KCl	pH = 1.3–6.3	MPL	Pavlov and Lazarov (1958a, 1958b)

<sup>a</sup> Compounds have been written in the form used by the authors. Correspondences:  $\text{HSbO}_3 \approx \text{H}[\text{Sb}(\text{OH})_6] \approx \text{Sb}(\text{OH})_5$ ;  $\text{SbO}_2^+ \approx \text{Sb}(\text{OH})_4^+$ ;  $\text{SbO}_3^- \approx \text{Sb}(\text{OH})_6^-$ ;  $\text{HSbO}_2 \approx \text{H}_3\text{SbO}_3 \approx \text{Sb}(\text{OH})_3 \approx \text{SbO}(\text{OH})$ ;  $\text{SbO}^+ \approx \text{Sb}(\text{OH})_2^+$ ;  $\text{SbO}_2^- \approx \text{Sb}(\text{OH})_4^-$ .

<sup>b</sup> Value reproduced in Hogfeldt (1982).

<sup>c</sup> Value reproduced in Bond and Hefter (1980). Background electrolyte not given.

<sup>d</sup> Values used by Bond and Hefter (1980) to calculate values for the corresponding stepwise constants.

<sup>e</sup> Value recommended in Martell et al. (1993). Background electrolyte not given.

<sup>f</sup> Value reproduced in Sillén and Martell (1964).

Table A6. Published antimony-sulfide stability constants.

Reaction <sup>a</sup>	log <i>K</i>	<i>T</i> (°C)	Conditions	Solid	Technique	Reference
$\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3 + 3\text{H}^+ + 3\text{HS}^-$	-53.11	25		—	Reinterpretation of Spycher and Reed (1989) published solubility data <sup>b</sup>	
$\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{Sb}_2\text{S}_4^{2-} + \text{H}^+$	-14.00	25				
$\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{HSb}_2\text{S}_4^-$	-2.50	25				
	-1.80	50				
$\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- + \text{H}^+ = \text{H}_2\text{Sb}_2\text{S}_4$	0.25	25				
$\text{HSb}_2\text{S}_4^- = \text{Sb}_2\text{S}_4^{2-} + \text{H}^+$	11.50	25				
$\text{Sb}_2\text{S}_3(\text{s}) + \text{H}_2\text{S} = \text{H}_2\text{Sb}_2\text{S}_4$	-5.15	25	Variable (0.01 <i>m</i> S)	Crystall.	MSL	Krupp (1988)
$\text{Sb}_2\text{S}_3(\text{s}) + \text{H}_2\text{S} = \text{HSb}_2\text{S}_4^- + \text{H}^+$	-10.06					
$\text{Sb}_2\text{S}_3(\text{s}) + \text{H}_2\text{S} = \text{Sb}_2\text{S}_4^{2-} + 2\text{H}^+$	-19.58					
$\text{H}_2\text{Sb}_2\text{S}_4 = \text{HSb}_2\text{S}_4^- + \text{H}^+$	-4.91					
$\text{HSb}_2\text{S}_4^- = \text{Sb}_2\text{S}_4^{2-} + \text{H}$	-9.52					
$\text{Sb}_2\text{S}_3(\text{s}) + 6\text{H}_2\text{O} = 2\text{Sb}(\text{OH})_3 + 3\text{H}_2\text{S}$	-37.31	25	Variable (10 <sup>-4</sup> –0.006 <i>m</i> H <sub>2</sub> S) pH = 3.2–9	Crystall.	Calculation from <i>T</i> Kolpakova (1982) dependence data	
	-36.54	30				
	-33.69	50				
$\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{HSb}_2\text{S}_4^-$	-2.31	25				
	-2.09	30				
	-1.30	50				
$\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- = \text{HSb}_2\text{S}_4^-$	-2.4	25		—	Reinterpretation of Kolpakova (1971) Babko and Lisetskaya (1956) and Akkeret (1953) data	
$2\text{Sb}_2\text{S}_3(\text{s}) + \text{HS}^- + \text{OH}^- = \text{Sb}_4\text{S}_7^{2-} + \text{H}_2\text{O}$	0.7 <sup>d</sup>	25	Variable (0.45–7.16% (w) Na <sub>2</sub> S) pH > 12 <sup>c</sup>	Crystall.	MSL	Arntson et al. (1966)
$0.5\text{Sb}_2\text{S}_3(\text{s}) + \text{H}_2\text{O} + \text{H}^+ = \text{SbS}_2$	-13.9	25	Infinite dilution	—	EFEF	Sillén and Martell (1964) (personal communication)
$0.5\text{Sb}_2\text{S}_3(\text{s}) + 3\text{H}_2\text{O} = \text{Sb}(\text{OH})_3 + 1.5\text{H}_2\text{S}(\text{g})$	-14.7					
$\text{Sb}_2\text{S}_3(\text{s}) + \text{S}^{2-} = \text{Sb}_2\text{S}_4^{2-}$	2.1 <sup>e</sup>	30	Variable (0.03–0.06 mol/L Na <sub>2</sub> S) pH = 12.1–13.3	Colloidal	MSL	Dubey and Ghosh (1962)
$\text{Sb}_2\text{S}_4^{2-} + \text{H}_2\text{O} = \text{Sb}_2\text{S}_3 + \text{OH}^- + \text{HS}^-$	-1.16					
$0.5\text{Sb}_2\text{S}_3(\text{s}) + 0.5\text{S}^{2-} = \text{SbS}_2^-$ (pH 8–9)	0.45 <sup>e</sup>	20	Variable (0.04 <i>m</i> H <sub>2</sub> S, no sulfide)	Colloidal	MSL	Babko and Lisetskaya (1956)
$\text{Sb}_2\text{S}_3(\text{s}) + 2\text{OH}^- = \text{SbS}_2^- + \text{SbS}(\text{OH})_2^-$ (pH 10–11)	-1.10 <sup>e</sup>					
$0.5\text{Sb}_2\text{S}_3(\text{s}) + 1.5\text{S}^{2-} = \text{SbS}_3^{3-}$	0.89 <sup>e</sup>	25	0.005–0.1 <i>m</i> H <sub>2</sub> S, K <sub>2</sub> S pH = 1.9–12.3 Results at infinite dilution	Amorphous	MSL	Akeret (1953)
$\text{Sb}_2\text{S}_3(\text{s}) + 2\text{HS}^- = 2\text{SbS}_2^-$	-2.03 <sup>f</sup>					

Table A6. continued

Reaction	log <i>K</i>	<i>T</i> (°C)	Conditions	Solid	Technique	Reference
$\text{Sb}_2\text{S}_3(\text{s}) = \text{Sb}^{3+} + 2\text{S}^{2-}$	-92.8 <sup>e,g,h</sup>					
$0.5\text{Sb}_2\text{S}_3(\text{s}) + 3\text{H}^+ + 4\text{Cl}^- = \text{SbCl}_4^- + 1.5\text{H}_2\text{S}$	-12.24 <sup>e</sup>					
$0.5\text{Sb}_2\text{S}_3(\text{s}) + 3\text{OH}^- = 0.5\text{SbS}_3^{3-} + 0.5\text{SbO}_3^{3-} + 1.5\text{H}_2\text{O}$	4.31 <sup>i</sup>					
$2\text{SbO}^+ + 3\text{H}_2\text{S}(\text{g}) = \text{Sb}_2\text{S}_3(\text{s}) + 2\text{H}_2\text{O} + 2\text{H}^+$ $\Delta G = -38$ kcal		25	Infinite dilution	—	EFEF	Latimer (1952)

<sup>a</sup>Compounds have been written in the form used by the authors. Correspondances:  $\text{HSbO}_3 \approx \text{H}[\text{Sb}(\text{OH})_6] \approx \text{Sb}(\text{OH})_5$ ;  $\text{SbO}_2^+ \approx \text{Sb}(\text{OH})_4^+$ ;  $\text{SbO}_3^- \approx \text{Sb}(\text{OH})_6^-$ ;  $\text{HSbO}_2 \approx \text{H}_3\text{SbO}_3 \approx \text{Sb}(\text{OH})_3 \approx \text{SbO}(\text{OH})$ ;  $\text{SbO}^+ \approx \text{Sb}(\text{OH})_2^+$ ;  $\text{SbO}_2^- \approx \text{Sb}(\text{OH})_4^-$ .

<sup>b</sup> Values in Spycher and Reed (1989) were discussed by Krupp (1990). See also reply (Spycher and Reed, 1990).

<sup>c</sup>Not stated by the authors but deduced from other conditions of the experiments.

<sup>d</sup> Value reproduced in Sillén and Martell (1971).

<sup>e</sup> Value reproduced in Sillén and Martell (1964).

<sup>f</sup> Value quoted in Sillén and Martell (1964) as -2.33.

<sup>g</sup> Value reproduced in Kotrly and Sucha (1985).

<sup>h</sup> Probable source for the value recommended for the logarithm of the formation constant  $[\text{Sb}(\text{OH})_3]^2[\text{S}]^3/[\text{Sb}_2\text{S}_3(\text{s})]$  (-90.8, at 25°C and infinite dilution) in Smith and Martell (1976). More recently, Martell et al. (1993) recommend the value -29.4 for  $[\text{Sb}(\text{OH})_3]^2[\text{H}_2\text{S}]^3/[\text{Sb}_2\text{S}_3(\text{s})]$ .

<sup>i</sup> Value quoted in Sillén and Martell (1964) as 4.015.