

**CHEMICAL**

VOLUME

**THERMODYNAMICS**

**12**

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**CHEMICAL  
THERMODYNAMICS  
OF TIN**

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# CHEMICAL THERMODYNAMICS OF TIN

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Vol. 11. Chemical Thermodynamics of Thorium, OECD Nuclear Energy Agency Data Bank, Eds., OECD Publications, Paris, France, (2008).



# Preface

This volume is the 12<sup>th</sup> in the “Chemical Thermodynamics” series edited and produced by the OECD Nuclear Energy Agency (NEA). It is a critical review of the thermodynamic properties of tin, its compounds and aqueous complexes, initiated by the Management Board of the NEA Thermochemical Database Project Phase III (NEA TDB III). The European members of the TDB Sn Review Team – Wolfgang Voigt (Freiberg University of Mining and Technology, Germany), Tamás Gajda (University of Szeged, Hungary) and Heinz Gamsjäger as Chairman (Montanuniversität Leoben, Austria) – first met at the NEA in Issy-les-Moulineaux (France) in September 2004. The overseas members – Surendra K. Saxena (Florida International University, Miami, United States) and James Sangster (Sangster Research Laboratories, Montreal, Canada) participated in this kickoff meeting via phone and video link. Four subsequent plenary meetings took place at the NEA in March 2005, October 2005, March 2006 and October 2006. The latter was held in conjunction with the TDB III Executive Group Meeting on 25 October and the TDB III Management Board Meeting on 26-27 October 2006. In these meetings the Review Team reported that key values on Sn<sup>4+</sup> formation and the redox couple Sn<sup>4+</sup>/Sn<sup>2+</sup> were lacking. Moreover, essential formation data on Sn(IV) chlorido and hydroxido complexes were also lacking. Therefore the Review Team submitted a proposal to the Management Board requesting to fund an experimental programme to obtain values for the most important critical data, while the already completed sections dealing with solids and gases were sent to peer review. The Management Board agreed and the experimental investigation was carried out under the leadership of Tamás Gajda at the University of Szeged Department of Inorganic and Analytical Chemistry. From 7 to 10 August 2008 the solution chemistry group comprising Wolfgang Voigt, Tamás Gajda and Heinz Gamsjäger met at Montanuniversität Leoben to include the results of the experimental study in the tin draft. The publication of these results, mandatory by NEA standards for including new data in chemical thermodynamics volumes, appeared in 2009. Heinz Gamsjäger presented these results at the meeting of the TDB IV Executive Group on 19 May 2010 in Karlsruhe.

Hans Wanner participated in meetings of the Review Team as the designated member of the Executive Group until he retired from this position in 2007. At the NEA Data Bank the responsibility for the overall co-ordination of the project was placed with Federico Mompean (from its initiation in 2004 to 2007), with Mireille Defranceschi (2008 to 2010) and Jane Perrone (2011). Jane Perrone was in charge of the preparation

of the successive drafts, updating the NEA Thermodynamic Database and editing the book in its present final form.

Primary responsibility for the different chapters was divided as follows. James Sangster and Surendra Saxena assessed the thermodynamic properties of solid and gaseous compounds, while Wolfgang Voigt, Tamás Gajda and Heinz Gamsjäger were in charge of the aqueous chemistry. Surendra Saxena drafted the sections on solid oxides, hydrides, halides, pnictides and selected minerals. James Sangster prepared the sections on elemental tin, gaseous compounds of all groups and solid compounds not treated by Surendra Saxena. Tamás Gajda drafted the sections on hydrolysis of Sn(II) and Sn(IV) and the sections on aqueous Sn(II) and Sn(IV) complexes. Wolfgang Voigt prepared the sections on solubilities of all groups. The chairman drafted the sections on simple aqua ions and those on solubilities of Sn(II) as well as Sn(IV) oxides and hydroxides. The key values for Sn(IV) which were lacking prompted close co-operation of the solution chemistry group. This contributed favourably to the final solution of the problem and to the quality of the solution chemistry section.

It is worth noting that the selection of key values, *e.g.*, for  $\text{Sn}^{2+}$ , revealed gaps in our knowledge which may stimulate rewarding projects on the experimental thermodynamics of tin compounds.

Leoben, Austria, May 2012

Heinz Gamsjäger, Chairman



# Acknowledgements

For the preparation of this book, the authors have received financial support from the NEA TDB Phase III Project. The following organisations take part in the project:

ONDRAF/NIRAS, Belgium  
NWMO, Canada  
RAWRA, Czech Republic  
POSIVA, Finland  
ANDRA, France  
CEA, France  
KIT, Germany  
JAEA, Japan  
ENRESA, Spain  
SKB, Sweden  
SKI, Sweden  
ENSI, Switzerland  
NAGRA, Switzerland  
PSI, Switzerland  
NDA, United Kingdom  
DoE, United States

Heinz Gamsjäger would like to express his gratitude to the Lehrstuhl für Physikalische Chemie of the Montanuniversität Leoben for having provided the infrastructure necessary for his contributions to this project. Tamás Gajda gratefully acknowledges the technical support of the Department of Inorganic and Analytical Chemistry at the University of Szeged.

The authors thank the TDB III Management Board for funding the experimental programme which enabled them to determine the standard potential of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple which thermodynamically links Sn(II) and Sn(IV) chemistry. Heinz Gamsjäger greatly appreciates Robert Lemire's continuous willingness to share his expertise and to give invaluable advice in all TDB review matters.

The unceasing efforts of Federico Mompean are greatly appreciated. He acted as co-ordinator for the TDB Sn project during the time the first version of this book was assembled and drafted and the part on solid and gaseous compounds of tin was edited

for peer review. The authors are also indebted to Mireille Defranceschi who succeeded in the position as co-ordinator from 2008 to 2010. A special acknowledgement goes to Jane Perrone who accompanied the evolution of the tin review from start to finish as volume editor and finally as series editor and project co-ordinator. She provided a pleasant working climate at TDB Sn meetings and harmonised several author contributions, prepared in many different formats, with admirable alertness and scientific competence.

The entire manuscript has undergone a peer review by an independent, international group of reviewers, according to the procedures in the TDB-6 Guideline, available from the NEA. The peer reviewers have seen and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the NEA. The peer reviewers were Prof. Erik Rosén, University of Umeå, Sweden for the section on solid and gaseous compounds of tin and Prof. Willis Forsling, University of Luleå, Sweden for the section on solution chemistry.

Their valuable contributions to this review are gratefully acknowledged.

## Editor's note

This is the 12<sup>th</sup> volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. This volume is devoted to the inorganic species and compounds of tin. The tables contained in Chapters III and IV list the currently selected thermodynamic values within the NEA TDB Project. The database system developed at the NEA Data Bank, see Section II.6, assures consistency among all the selected and auxiliary data sets.

The recommended thermodynamic data are the result of a critical assessment of published information. The values in the auxiliary data set, see Tables IV-1 and IV-2 have been adopted from CODATA key values or have been critically reviewed in this or earlier volumes of the series.

**How to contact the NEA TDB Project**

Information on the NEA and the TDB Project, online access to selected data and computer programs, as well as many documents in electronic format are available at [www.oecd-nea.org](http://www.oecd-nea.org).

To contact the TDB Project coordinator and the authors of the review reports, send comments on the TDB reviews, or to request further information, please send e-mail to [tdb@oecd-nea.org](mailto:tdb@oecd-nea.org). If this is not possible, write to:

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# **Part 1**

## **Introductory material**



# Chapter I

## Introduction

### I.1 Background

The modelling of the behaviour of hazardous materials under environmental conditions is among the most important applications of natural and technical sciences for the protection of the environment. In order to assess, for example, the safety of a waste deposit, it is essential to be able to predict the eventual dispersion of its hazardous components in the environment (geosphere, biosphere). For hazardous materials stored in the ground or in geological formations, the most probable transport medium is the aqueous phase. An important requirement for predicting the pathways and rates of aqueous transport of potential contaminants is therefore the quantitative prediction of the reactions that are likely to occur between hazardous waste dissolved or suspended in ground water, and the surrounding rock material, in order to estimate the quantities of waste that can be transported in the aqueous phase. It is thus essential to know the relative stabilities of the compounds and complexes that may form under the relevant conditions. This information is often provided by speciation calculations using chemical thermodynamic data. The local conditions, such as ground water and rock composition or temperature, may not be constant along the migration paths of hazardous materials, and fundamental thermodynamic data are the indispensable basis for dynamic modelling of the chemical behaviour of hazardous waste components.

In the field of radioactive waste management, the hazardous material consists to a large extent of actinides and fission products from nuclear reactors, in addition to lesser amounts from other sources such as waste from medicine, industry and research facilities. The scientific literature on thermodynamic data, mainly on equilibrium constants and redox potentials in aqueous solution, has been contradictory in a number of cases, especially in the actinide chemistry. A critical and comprehensive review of the available literature is necessary in order to establish a reliable thermochemical data base that fulfils the requirements of a proper modelling of the behaviour of the actinide and fission products in the environment.

Between 1963 and 1967, the International Atomic Energy Agency (IAEA) in Vienna published three technical reports with thermochemical assessments of the nuclear fuel systems: U-C and Pu-C [1963IAE],  $\text{UO}_2$  and related phases [1965IAE], and Pu-O and U-Pu-O [1967IAE]. These reports were followed by nine special issues of *Atomic Energy Review* with compilations of physicochemical properties of compounds and alloys of elements important in reactor technology: Pu, Nb, Ta, Be, Th, Zr, Mo, Hf

and Ti. In 1976, the IAEA also started the publication of the series “The Chemical Thermodynamics of Actinide Elements and Compounds”, oriented towards nuclear engineers and scientists. This international effort has resulted in the publication of ten volumes, each concerning the thermodynamic properties of a given type of compounds for the entire actinide series. These reviews cover the literature up to about 1984. The last volume in this series, Part 12: The Actinide Aqueous Inorganic Complexes [1992FUG/KHO] appeared in 1992. Unfortunately, four scheduled reviews in the IAEA series of importance for radioactive waste management were never published (including, for example, Part 10: The Actinide Oxides and Part 14: Aqueous Organic Complexes).

The Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency recognised the need for an internationally acknowledged, high-quality thermochemical database for application in the safety assessment of radioactive waste disposal, and undertook the development of the NEA Thermochemical Data Base (TDB) project [1985MUL], [1988WAN], [1991WAN]. The RWMC assigned a high priority to the critical review of relevant chemical thermodynamic data of compounds and complexes for this area containing the actinides uranium, neptunium, plutonium and americium, as well as the fission product technetium. The first four books in this series on the chemical thermodynamics of uranium [1992GRE/FUG], americium [1995SIL/BID], technetium [1999RAR/RAN] and neptunium and plutonium [2001LEM/FUG] originated from this initiative.

In 1998, Phase II of the TDB Project (TDB-II) was started to provide for the further needs of the radioactive waste management programs by updating the existing database and applying the TDB review methodology to other elements (nickel, selenium, zirconium) and to simple organic compounds and complexes. In TDB-II the overall objectives were set by a Management Board, integrated by the representatives of 17 organisations from the field of radioactive waste management. These participating organisations, together with the NEA, provided financial support for TDB-II. The TDB-II Management Board was assisted in technical matters by a group of experts in chemical thermodynamics (the Executive Group). The NEA acted in this phase as Project Co-ordinator ensuring the implementation of the Project Guidelines and liaising with the Review Teams. Five publications resulted from TDB-II: the update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium [2003GUI/FAN], the books on chemical thermodynamics of nickel [2005GAM/BUG], selenium [2005OLI/NOL] and zirconium [2005BRO/CUR] and the volume devoted to compounds and complexes of the above mentioned metals with selected organic ligands [2005HUM/AND].

In 2003, TDB III, the current third phase of the Project was started with an organisation and participation similar to the one adopted for TDB-II. Three reviews are contemplated: the volume devoted to the inorganic species and compounds of thorium [2008RAN/FUG] has been published as volume 11 of the Chemical Thermodynamics



Series, that reported in the present volume dealing with inorganic compounds and complexes of tin and one further volume dealing with iron. In addition, an expert group was constituted to prepare a state-of-the-art report on the chemical thermodynamics of solid solutions of interest in radioactive waste management. This report [2007BRU/BOS] has been published as volume 10 of the Chemical Thermodynamics Series. The current volume, twelfth in the Series, is therefore the third deliverable from this phase of the NEA TDB Project.

The earlier eleven volumes of the series are listed in the frontispiece of this volume; it may be noted that first two volumes [1992GRE/FUG], [1995SIL/BID] and the companion volume on the modelling of aqueous solutions [1997ALL/BAN], are available without charge from the NEA.

Simultaneously with the NEA TDB project, other reviews on the physical and chemical properties of actinides have appeared, including the book by Cordfunke *et al.* [1990COR/KON], the series edited by Freeman *et al.* [1984FRE/LAN], [1985FRE/LAN], [1985FRE/KEL], [1986FRE/KEL], [1987FRE/LAN], and [1991FRE/KEL], Part 12 of the IAEA review series by Fuger *et al.* [1992FUG/KHO] mentioned above and the two comprehensive books by Katz *et al.* [1986KAT/SEA] and Morss *et al.* [2006MOR/EDE] (particularly Chapter 19 [2006KON/MOR]). All the compilations mentioned, although much less detailed than the NEA reviews (particularly with regard to the detailed documentation and discussion of published data) are both an important source of information, and a complement to the thermodynamic data contained in this volume (with due regard to consistency).

## I.2 Focus of the review

The first and most important step in the modelling of chemical reactions is to decide whether they are controlled by chemical thermodynamics or kinetics, or possibly by a combination of the two. This also applies to the modelling of more complex chemical systems and processes, such as waste repositories of various kinds, the processes describing transport of toxic materials in ground and surface water systems, global geochemical cycles, *etc.*

As outlined in the previous section, the focus of the critical review presented in this book is on the thermodynamic data of tin relevant to the safety assessment of radioactive waste repositories in the geosphere. This includes the release of waste components from the repository into the geosphere (*i.e.*, its interaction with the waste container and the other near-field materials) and their migration through the geological formations and the various compartments of the biosphere. As ground waters and pore waters are the transport media for the waste components, the knowledge of the thermodynamics of the corresponding elements in waters of various compositions is of fundamental importance.

The present review therefore puts much weight on the assessment of the thermodynamics of tin in aqueous solution at ambient temperatures and makes independent analyses of the available literature in this area. Appendix B describes in detail the Specific Ion Interaction Theory, which is the model selected in the NEA TDB review series to describe the ionic interactions between components in aqueous solutions. This allows the general and consistent use of the selected data for modelling purposes, regardless of the type and composition of the ground water.

The interactions between solid compounds and aqueous solutions are as important as the interactions within the aqueous solution, because the solid materials in the geosphere control the chemistry of the ground water, and also contribute to the overall solubilities of key elements. The present review therefore also considers the thermodynamic data of many solid tin compounds.

This book contains a summary and critical reviews of the thermodynamic data on compounds and complexes containing tin, as reported in the available chemical literature up to the end of 2009 but a few more recent references are also included. A large number of primary references are discussed separately in Appendix A.

Although the focus of this review is on tin, it is necessary to use data on a number of other species during the evaluation process that lead to the recommended data. These auxiliary data are taken both from the publication of CODATA Key Values [1989COX/WAG] and from the evaluation of additional auxiliary data in the other volumes of this series detailed above, and their use is recommended by this review. Care has been taken that all the selected thermodynamic data at standard conditions (*cf.* Section II.3) and 298.15 K are internally consistent. For this purpose, special software has been developed at the NEA Data Bank that is operational in conjunction with the NEA TDB data base system, *cf.* Section II.6. In order to maintain consistency in the application of the values selected by this review, it is essential to use these auxiliary data when calculating equilibrium constants involving tin compounds and complexes.

The present review does not include any compounds or complexes of elements in Groups 3 to 13 of the Periodic Table (which are mostly alloys), nor species containing organic ligands or species in non-aqueous solvents. Organic species were subject of the ninth volume in the NEA TDB series [2005HUM/AND], although this does not include any data for tin species.

### **I.3 Review procedure and results**

The objective of the present review is to present an assessment of the sources of published thermodynamic data in order to decide on the most reliable values and their uncertainties that can be recommended for modelling purposes. Experimental measurements published in the scientific literature are the main source for the selection

of recommended data. Previous reviews are not neglected, since they form a valuable source of critical information on the quality of primary publications. When necessary, experimental source data are re-evaluated by using chemical models which are either found to be more realistic than those used by the original author, or are consistent with subsequent information, or with side-reactions discussed in another section of the review (for example, data on solubilities of basic salts might need to be re-interpreted to take into account stoichiometry of the phase actually investigated).

Re-evaluation of literature values might be also necessary to correct for known systematic errors (for example, if complex formation was neglected in the original publication) or to make extrapolations to standard state conditions ( $I = 0$ ) by using the specific ion interaction (SIT) equations (*cf.* Appendix B). For convenience, these SIT equations are referred to in some places in the text as “the SIT”. In order to ensure that consistent procedures are used for the evaluation of primary data, a number of guidelines have been developed. They have been updated and improved since 1987, and their most recent versions are available at the NEA [1999WAN], [1999WAN/OST], [2000OST/WAN], [2000GRE/WAN], [2000WAN/OST]. Some of these procedures are also outlined in this volume, *cf.* Chapter II, Appendix B, and Appendix C. Parts of these sections, which were also published in earlier volumes in this series, have been revised in this review, particularly the Tables in Appendix B.

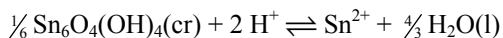
Once the critical review process in the NEA TDB project is completed, the resulting manuscript is reviewed independently by qualified experts nominated by the NEA. The independent peer review is performed according to the procedures outlined in the TDB-6 guideline [1999WAN]. The purpose of the additional peer review is to obtain an independent view of the judgements and assessments made by the primary reviewers, to verify assumptions, results and conclusions, and to check whether the relevant literature has been exhaustively considered. The independent peer review is performed by scientists having technical expertise in the subject matter to be reviewed.

The thermodynamic data selected in the present review (see Chapter III) refer to the reference temperature of 298.15 K and to standard conditions, *cf.* Section II.3. For the modelling of real systems it is, in general, necessary to recalculate the standard thermodynamic data to non-standard state conditions. For aqueous species a procedure for the calculation of the activity factors is thus required. As noted earlier, this review uses the approximate specific ion interaction method (SIT) for the extrapolation of experimental data to the standard state in the data evaluation process, and in some cases this requires the re-evaluation of original experimental values (solubilities, cell-potential data, *etc.*). For maximum consistency, the selected data presented in this review must always be used in conjunction with this method as described in Appendix B. The thermodynamic data selected in this review are provided with uncertainties representing the 95% confidence level. As discussed in Appendix C, there is no unique way to assign uncertainties, and the assignments made in this review are to a large extent based on the

subjective choice by the reviewers, supported by their scientific and technical experience in the corresponding area.

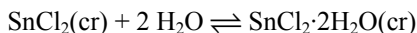
The quality of thermodynamic models cannot be better than the quality of the data on which they are based. The quality aspect includes both the numerical values of the thermodynamic data used in the model and the “completeness” of the chemical model used, *e.g.*, the inclusion of all the relevant dissolved chemical species and solid phases. For the user it is important to note that the selected data set presented in this review (Chapter III) is certainly not “complete” with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the main text (Chapters V to XI), and this information may be used as a basis for the assignment of future research priorities. Two examples for rewarding projects in experimental thermodynamics must suffice.

Thermodynamic data for  $\text{Sn}_6\text{O}_4(\text{OH})_4$ , hydroromarchite, a corrosion product of elemental tin are lacking. Investigation of the temperature dependent solubility according to the reaction



would lead to the standard Gibbs energy of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  formation, as well as to provisional values for its standard enthalpy and its entropy.

The standard entropy of hydration according to the reaction



with  $\Delta S_m^\circ = -31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  per mole of water is probably too negative. A re-investigation of  $S_m^\circ(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  and  $S_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})$  would resolve this problem.

# Chapter II

## Standards, conventions and contents of the tables

This chapter outlines and lists the symbols, terminology and nomenclature, the units and conversion factors, the order of formulae, the standard conditions, and the fundamental physical constants used in this volume. They are derived from international standards and have been specially adjusted for the TDB publications.

### II.1 Symbols, terminology and nomenclature

#### II.1.1 Abbreviations

Abbreviations are mainly used in tables where space is limited. Abbreviations for methods of measurement are listed in Table II-1.

Table II-1: Abbreviations for experimental methods.

---

aix	Anion exchange
AES	Atomic Emission Spectroscopy
cal	Calorimetry
chr	Chromatography
cix	Cation exchange
col	Colorimetry
con	Conductivity
cou	Coulometry
cry	Cryoscopy
dis	Distribution between two phases
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectroscopy
em	Electromigration
$E_{\text{cell}}$	Potential difference of an electrochemical cell

---

(Continued on next page)

Table II-1 (continued)

EPMA	Electron Probe Micro Analysis
EXAFS	Extended X-ray Absorption Fine Structure
FTIR	Fourier Transform Infra Red
IDMS	Isotope Dilution Mass-Spectroscopy
ir	Infrared
gl	Glass electrode
ise-x	Ion selective electrode with ion X stated
isop	Isopiestic
ix	Ion exchange
kin	Rate of reaction
LIBD	Laser Induced Breakdown Detection
MVD	Molar Volume Determination
NMR	Nuclear Magnetic Resonance
PAS	Photo Acoustic Spectroscopy
pol	Polarography
pot	Potentiometry
prx	Proton relaxation
qh	Quinhydrone electrode
red	$E_{\text{cell}}$ with redox electrode
SEM	Scanning Electron Microscopy
sp	Spectrophotometry
sol	Solubility
TC	Transient Conductivity
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis
TLS	Thermal Lensing Spectrophotometry
Tj	Temperature jump
TRLFS	Time Resolved Laser Fluorescence Spectroscopy
UV	Ultraviolet
vlt	Voltammetry
XANES	X-ray Absorption Near Edge Structure
XRD	X-ray Diffraction
?	Method unknown to the reviewers

Other abbreviations may also be used in tables, such as SHE for the standard hydrogen electrode or SCE for the saturated calomel electrode. The abbreviation NHE has been widely used for the “normal hydrogen electrode”, which is by definition identical to the SHE. It should nevertheless be noted that NHE customarily refers to a standard state pressure of 1 atm, whereas SHE always refers to a standard state pressure of 0.1 MPa (1 bar) in this review.

## II.1.2 Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [1979WHI], [1993MIL/CVI], [2008COH/CVI]. They are summarised in Table II-2.

Table II-2: Symbols and terminology.

Symbols and terminology	
length	$l$
height	$h$
radius	$r$
diameter	$d$
volume	$V$
mass	$m$
relative atomic mass	$A_r$
molar mass	$M$
density (mass divided by volume)	$\rho$
molar surface area	$A$
time	$t$
frequency	$\nu$
wavelength	$\lambda$
internal transmittance (transmittance of the medium itself, disregarding boundary or container influence)	$T$
internal transmission density, (decadic absorbance): $\log_{10}(1/T_i)$	$A$
molar (decadic) absorption coefficient: $A/c_B l$	$\varepsilon$
relaxation time	$\tau$
Avogadro constant	$N_A$
relative molecular mass of a substance <sup>(a)</sup>	$M_r$
thermodynamic temperature, absolute temperature	$T$
Celsius temperature	$t$
(molar) gas constant	$R$
Boltzmann constant	$k_B$
Faraday constant	$F$
(molar) entropy	$S_m$
(molar) heat capacity at constant pressure	$C_{p,m}$
(molar) enthalpy	$H_m$
(molar) Gibbs energy	$G_m$
chemical potential of substance B	$\mu_B$
pressure	$p$
partial pressure of substance B: $x_B p$	$p_B$
fugacity of substance B	$f_B$

(Continued next page)

Table II-2 (continued)

Symbols and terminology	
fugacity coefficient: $f_B/p_B$	$\gamma_{f,B}$
amount of substance <sup>(b)</sup>	$n$
mole fraction of substance B:	$x_B$
molarity or concentration of a solute substance B (amount of B divided by the volume of the solution) <sup>(c)</sup>	$c_B, [B]$
molality of a solute substance B (amount of B divided by the mass of the solvent) <sup>(d)</sup>	$m_B$
factor for the conversion of molarity to molality of a solution: $m_B/c_B$	$\xi$
mean ionic molality <sup>(e)</sup> , $m_{\pm}^{(v_+ + v_-)} = m_+^{v_+} m_-^{v_-}$	$m_{\pm}$
activity of substance B <sup>(e)</sup>	$a_B$
activity coefficient, molality basis: $a_B/m_B$	$\gamma_B$
activity coefficient, concentration basis: $a_B/c_B$	$\gamma_B$
mean ionic activity <sup>(e)</sup> , $a_{\pm}^{(v_+ + v_-)} = a_+^{v_+} a_-^{v_-}$	$a_{\pm}$
mean ionic activity coefficient <sup>(e)</sup> , $\gamma_{\pm}^{(v_+ + v_-)} = \gamma_+^{v_+} \gamma_-^{v_-}$	$\gamma_{\pm}$
osmotic coefficient, molality basis	$\phi$
ionic strength: $I_m = 1/2 \sum_i m_i z_i^2$ or $I_c = 1/2 \sum_i c_i z_i^2$	$I$
SIT ion interaction coefficient between substance B <sub>1</sub> and substance B <sub>2</sub> )	$\varepsilon(B_1, B_2)$
stoichiometric coefficient of substance B (negative for reactants, positive for products)	$\nu_B$
general equation for a chemical reaction	$0 = \sum_B \nu_B B$
equilibrium constant <sup>(f)</sup>	$K$
charge number of an ion B (positive for cations, negative for anions)	$z_B$
charge number of a cell reaction	$n$
Potential difference of an electrochemical cell	$E$
pH = $-\log_{10}[a_{H^+} / (\text{mol} \cdot \text{kg}^{-1})]$	pH
molar conductivity	$\Lambda$
molar conductivity at $I=0$	$\Lambda_0$
superscript for standard state <sup>(g)</sup>	$^\circ$

a: Ratio of the average mass per formula unit of a substance to  $\frac{1}{12}$  of the mass of an atom of nuclide  $^{12}\text{C}$ .

b: cf. sections 1.2 and 3.6 of the IUPAC manual [1979WHI].

c: This quantity is called "amount-of-substance concentration" in the IUPAC manual [1979WHI]. A solution with a concentration equal to  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  is called a 0.1 molar solution or a 0.1 M solution.

d: A solution having a molality equal to 0.1 moles of solute per kg solvent is called a 0.1 molal solution or a 0.1 m solution.

e: For an electrolyte  $N_{\nu_+} X_{\nu_-}$  which dissociates into  $\nu_{\pm}$  ( $= \nu_+ + \nu_-$ ) ions, in an aqueous solution with molality  $m$ , the individual cationic molality and activity coefficient are  $m_+ (= \nu_+ m)$  and  $\gamma_+ (= a_+ / m_+)$ . A similar definition is used for the anionic symbols. Electrical neutrality requires that  $\nu_+ z_+ = \nu_- z_-$ .

f: Special notations for equilibrium constants are outlined in Section II.1.7. In some cases,  $K_c$  is used to indicate a concentration constant in molar units, and  $K_m$  a constant in molal units.

g: See Section II.3.1.

\*: In many places in this volume  $a_w$  has been used as synonym for  $a_{\text{H}_2\text{O}}$ .



### II.1.3 Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [1971JEN], [1977FER], [1990LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

- The formulae of co-ordination compounds and complexes are not enclosed in square brackets [1971JEN] (Rule 7.21). Exceptions are made in cases where square brackets are required to distinguish between co-ordinated and unco-ordinated ligands.
- The prefixes “oxy-” and “hydroxy-” are retained if used in a general way, *e.g.*, “gaseous uranium oxyfluorides”. For specific formula names, however, the IUPAC recommended citation [1971JEN] (Rule 6.42) is used, *e.g.*, “uranium(IV) difluoride oxide” for  $\text{UF}_2\text{O}(\text{cr})$ .

An IUPAC rule that is often not followed by many authors [1971JEN] (Rules 2.163 and 7.21) is recalled here: the order of arranging ligands in co-ordination compounds and complexes is the following: central atom first, followed by ionic ligands and then by the neutral ligands. If there is more than one ionic or neutral ligand, the alphabetical order of the symbols of the ligands determines the sequence of the ligands. For example,  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$  is standard,  $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$  is not recommended.

It is convenient to have a shorthand method of referring to an ionic medium where the anion concentration is kept constant, but the cation concentrations vary, since such solutions are often used to minimise changes in interionic attractions. For this we enclose the major cation in parentheses. For example, a solution described as “3.00 M (Na)ClO<sub>4</sub>” could be a mixture of 0.01 M Th(ClO<sub>4</sub>)<sub>4</sub> and 2.96 M NaClO<sub>4</sub> with a total perchlorate concentration of 3.00 M.

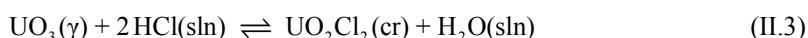
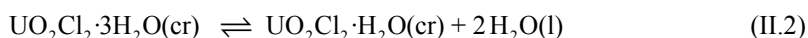
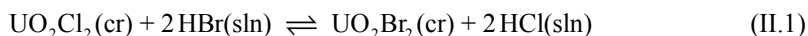
Abbreviations of names for organic ligands appear sometimes in formulae. Following the recommendations by IUPAC, lower case letters are used, and if necessary, the ligand abbreviation is enclosed within parentheses. Hydrogen atoms that can be replaced by the metal atom are shown in the abbreviation with an upper case “H”, for example:  $\text{H}_3\text{edta}^-$ , Am(Hedta)(s) (where edta stands for ethylenediaminetetraacetate).

### II.1.4 Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example,  $\text{UF}_4$  occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that are not provided with a phase designator are aqueous ions. They are the only charged species in this review since charged gases are not considered. The use of the phase designators is described below.

- The designator (l) is used for pure liquid substances, *e.g.*, H<sub>2</sub>O(l).
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, U(OH)<sub>4</sub>(aq), CO<sub>2</sub>(aq). Since ionic gases are not considered in this review, all ions may be assumed to be aqueous and are not designed with (aq). If a chemical reaction refers to a medium other than H<sub>2</sub>O (*e.g.*, D<sub>2</sub>O, 90% ethanol/10% H<sub>2</sub>O), then (aq) is replaced by a more explicit designator, *e.g.*, “(in D<sub>2</sub>O)” or “(sln)”. In the case of (sln), the composition of the solution is described in the text.
- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the difference in the designation of H<sub>2</sub>O in Eqs. (II.2) and (II.3). H<sub>2</sub>O(l) in Reaction (II.2) indicates that H<sub>2</sub>O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (II.3) involves an HCl solution, in which the thermodynamic properties of H<sub>2</sub>O(sln) may not be the same as those of the pure liquid H<sub>2</sub>O(l). In dilute solutions, however, this difference in the thermodynamic properties of H<sub>2</sub>O can be neglected, and H<sub>2</sub>O(sln) may be regarded as pure H<sub>2</sub>O(l).

Example:



- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.
- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses, *e.g.*, SiO<sub>2</sub>(quar) for quartz and SiO<sub>2</sub>(chal) for chalcedony. If there is no mineral name, the designator (cr) is replaced by a Greek letter preceding the formula and indicating the structural phase, *e.g.*, α-UF<sub>5</sub>, β-UF<sub>5</sub>.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound to which a thermodynamic quantity refers. The notation is in this case the same as outlined above. In an extended notation (*cf.* [1982LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G_m^\circ(\text{Na}^+, 298.15 \text{ K})$	standard molar Gibbs energy of formation of aqueous $\text{Na}^+$ at 298.15 K
$S_m^\circ(\text{UO}_2(\text{SO}_4)\cdot 2.5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$	standard molar entropy of $\text{UO}_2(\text{SO}_4)\cdot 2.5\text{H}_2\text{O}(\text{cr})$ at 298.15 K
$C_{p,m}^\circ(\text{UO}_3, \alpha, 298.15 \text{ K})$	standard molar heat capacity of $\alpha\text{-UO}_3$ at 298.15 K
$\Delta_f H_m(\text{HF}, \text{sln}, \text{HF}\cdot 7.8\text{H}_2\text{O})$	enthalpy of formation of HF diluted 1:7.8 with water.

### II.1.5 Processes

Chemical processes are denoted by the operator  $\Delta$ , written before the symbol for a property, as recommended by IUPAC [1982LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.7. The nature of the process is denoted by annotation of the  $\Delta$ , *e.g.*, the Gibbs energy of formation,  $\Delta_f G_m$ , the enthalpy of sublimation,  $\Delta_{\text{sub}} H_m$ , *etc.* The abbreviations of chemical processes are summarised in Table II-3.

Table II-3: Abbreviations used as subscripts of  $\Delta$  to denote the type of chemical process.

Subscript of $\Delta$	Chemical process
at	separation of a substance into its constituent gaseous atoms (atomisation)
dehyd	elimination of water of hydration (dehydration)
dil	dilution of a solution
f	formation of a compound from its constituent elements
fus	melting (fusion) of a solid
hyd	addition of water of hydration to an unhydrated compound
mix	mixing of fluids
r	chemical reaction (general)
sol	process of dissolution
sub	sublimation (evaporation) of a solid
tr	transfer from one solution or liquid phase to another
trs	transition of one solid phase to another
vap	vaporisation (evaporation) of a liquid

The most frequently used symbols for processes are  $\Delta_f G$  and  $\Delta_f H$ , the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (*cf.* Table II-6).

## II.1.6 Nomenclature in log terms

It is of course clear that the arguments used in log functions must be dimensionless, and this practice has been used in writing pressures, usually as  $\log_{10} p/\text{bar}$ . However, since the units of the equilibrium constants,  $K_m$  and  $K_c$ , are frequently quite cumbersome, they have been omitted in the log terms of these ( $\log_{10} K_m$  and  $\log_{10} K_c$ ) to facilitate reading of the text.

## II.1.7 Equilibrium constants

IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA TDB Project has therefore adopted the conventions that have been used in the work *Stability Constants of Metal Ion Complexes* by Sillén and Martell [1964SIL/MAR], [1971SIL/MAR]. An outline is given in the paragraphs below. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It may sometimes be preferable to indicate the number of the reaction to which the data refer, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium:



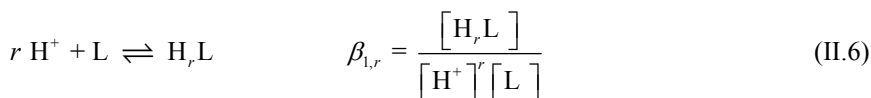
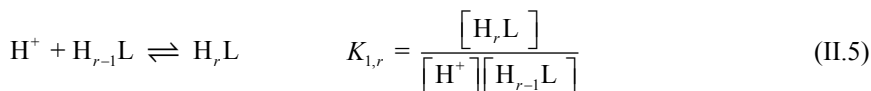
both  $\beta_{q,m}$  and  $\beta$  (II.4) would be appropriate, and  $\beta_{q,m}$  (II.4) is accepted, too. Note that, in general,  $K$  is used for the consecutive or stepwise formation constant, and  $\beta$  is used for the cumulative or overall formation constant. In the following outline, charges are only given for actual chemical species, but are omitted for species containing general symbols (M, L).

The expressions in sub-Sections II.1.7.1.1 through II.1.7.1.4 are expressed in terms of (amount substance) concentrations (*i.e.*,  $[X] \equiv c_X$  and the constants are  $K_c$ ; *cf.* footnote *f* to Table II-2), but parallel nomenclature has been used in the rest of the review for equilibria expressed using molalities ( $K_m$ ) or using activities in thermodynamic equilibrium constants ( $K^\circ$ ). The units here for

$$K_c = \prod_{\text{B}} c^{\nu_{\text{B}}}$$

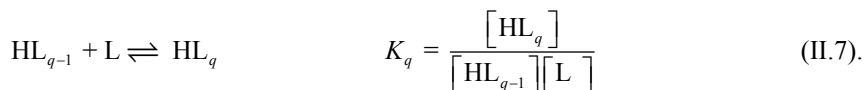
are  $(\text{mol} \cdot \text{dm}^{-3})^{\sum_{\text{B}} \nu_{\text{B}}}$ .

### II.1.7.1 Protonation of a ligand

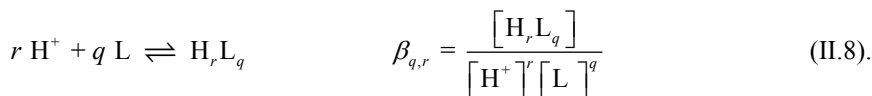


This notation has been proposed and used by Sillén and Martell [1964SIL/MAR], but it has been simplified later by the same authors [1971SIL/MAR] from  $K_{1,r}$  to  $K_r$ .

For the addition of a ligand, the notation shown in Eq. (II.7) is used.

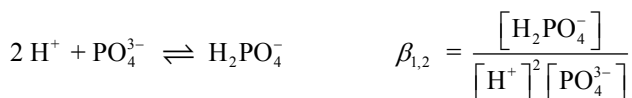


Eq. (II.8) refers to the overall formation constant of the species  $\text{H}_r\text{L}_q$ .

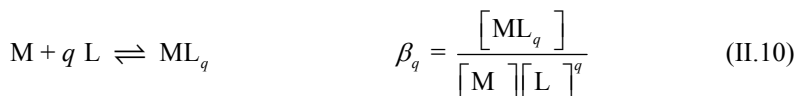
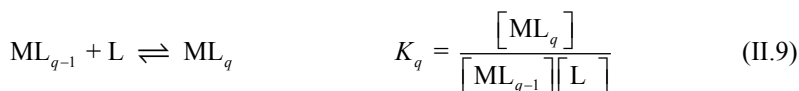


In Eqs. (II.5), (II.6) and (II.8), the second subscript  $r$  can be omitted if  $r = 1$ , as shown in Eq. (II.7).

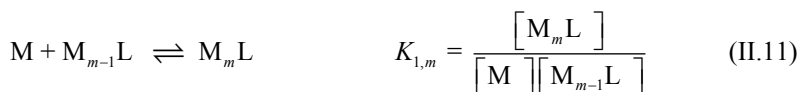
Example:



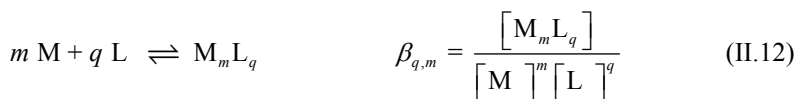
### II.1.7.2 Formation of metal complexes



For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq. (II.5):



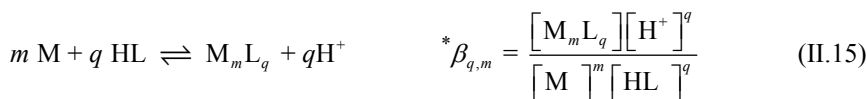
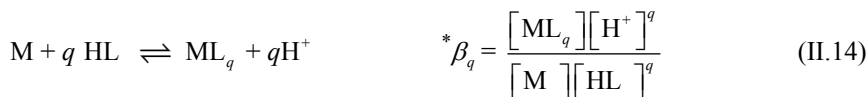
Eq. (II.12) refers to the overall formation constant of a complex  $\text{M}_m\text{L}_q$ .



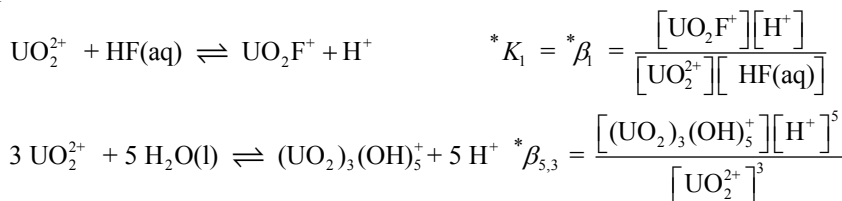
The second index can be omitted if it is equal to 1, *i.e.*,  $\beta_{q,m}$  becomes  $\beta_q$  if  $m = 1$ . The formation constants of mixed ligand complexes are not indexed. In this case,

it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

It has sometimes been customary to use negative values for the indices of the protons to indicate complexation with hydroxide ions,  $\text{OH}^-$ . This practice is not adopted in this review. If  $\text{OH}^-$  occurs as a reactant in the notation of the equilibrium, it is treated like a normal ligand L, but in general formulae the index variable  $n$  is used instead of  $q$ . If  $\text{H}_2\text{O}$  occurs as a reactant to form hydroxide complexes,  $\text{H}_2\text{O}$  is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs. (II.13) to (II.15) using  $n$  as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex  $\text{M}_m\text{L}_q\text{H}_r$ . In many experiments, the formation constants of metal ion complexes are determined by adding a ligand in its protonated form to a metal ion solution. The complex formation reactions thus involve a deprotonation reaction of the ligand. If this is the case, the equilibrium constant is supplied with an asterisk, as shown in Eqs. (II.13) and (II.14) for mononuclear and in Eq. (II.15) for polynuclear complexes.



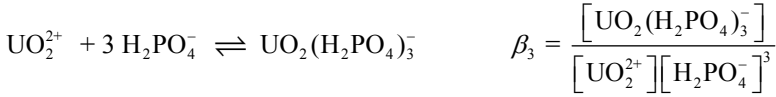
Example:



Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added and co-ordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (II.16).

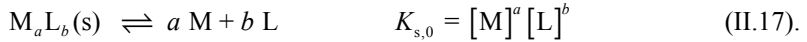


Example:

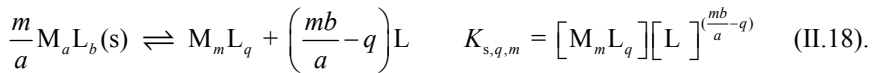


### II.1.7.3 Solubility constants

Conventionally, equilibrium constants involving a solid compound are denoted as “solubility constants” rather than as formation constants of the solid. An index “s” to the equilibrium constant indicates that the constant refers to a solubility process, as shown in Eqs. (II.17) to (II.19).



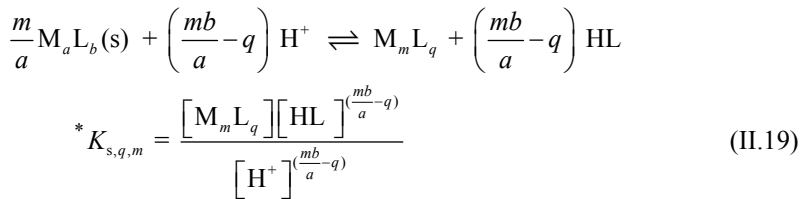
$K_{s,0}$  is the conventional solubility product, and the subscript “0” indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq. (II.12) is used:



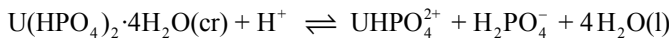
Example:



Similarly, an asterisk is added to the solubility constant if it simultaneously involves a protonation equilibrium:



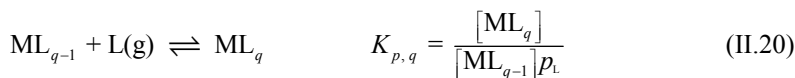
Example:



$$*K_{s,1,1} = *K_{s,1} = \frac{[\text{UHPO}_4^{2+}][\text{H}_2\text{PO}_4^-]}{[\text{H}^+]}$$

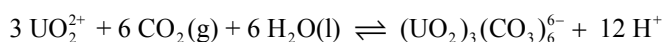
### II.1.7.4 Equilibria involving the addition of a gaseous ligand

A special notation is used for constants describing equilibria that involve the addition of a gaseous ligand, as outlined in Eq. (II.20).



The subscript “*p*” can be combined with any other notations given above.

Example:



$$^* \beta_{p,6,3} = \frac{[(\text{UO}_2)_3(\text{CO}_3)_6^{6-}][\text{H}^+]^{12}}{[\text{UO}_2^{2+}]^3 p_{\text{CO}_2}^6}$$



$$^* K_{p,s,2} = \frac{[\text{UO}_2(\text{CO}_3)_2^{2-}][\text{H}^+]^2}{p_{\text{CO}_2}}$$

In cases where the subscripts become complicated, it is recommended that *K* or *β* be used with or without subscripts, but always followed by the equation number of the equilibrium to which it refers.

### II.1.7.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, *E*, which is identical to the potential difference of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE<sup>1</sup>, in accordance with the “1953 Stockholm Convention” [1993MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, H<sub>2</sub>(g) is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and H<sup>+</sup> is at unit activity. The sign of the electrode potential, *E*, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential, *E*<sup>o</sup>, *i.e.*, the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section II.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change Δ<sub>r</sub>*G*<sub>m</sub><sup>o</sup> and the standard (or thermodynamic) equilibrium constant *K*<sup>o</sup> as outlined in Eq. (II.21):

<sup>1</sup> The definitions of SHE and NHE are given in Section II.1.1.

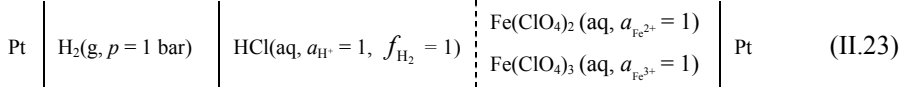


$$E^\circ = -\frac{1}{nF} \Delta_r G_m^\circ = \frac{RT}{nF} \ln K^\circ \quad (\text{II.21})$$

and the potential,  $E$ , is related to  $E^\circ$  by:

$$E = E^\circ - (RT/nF) \sum \nu_i \ln a_i. \quad (\text{II.22})$$

For example, for the hypothetical galvanic cell:



where  $\left| \right|$  denotes a liquid junction and  $\left| \right.$  a phase boundary, the reaction is:



Formally Reaction (II.24) can be represented by two half cell reactions, each involving an equal number of electrons, (designated “ $e^-$ ”), as shown in the following equations:



The terminology is useful, although it must be emphasised “ $e^-$ ” here does not represent the hydrated electron.

Equilibrium (II.26) and Nernst law can be used to introduce  $a_{e^-}$  :

$$E = E^\circ (\text{II.26}) + \frac{RT}{F} \ln(\sqrt{f_{\text{H}_2}} / (a_{\text{H}^+} \cdot a_{e^-})) \quad (\text{II.27})$$

According to the SHE convention  $E^\circ (\text{II.26}) = 0$ ,  $f_{\text{H}_2} = 1$ ,  $a_{\text{H}^+} = 1$ , hence

$$E = -\frac{RT}{F} \ln a_{e^-} \quad (\text{II.28})$$

This equation is used to calculate a numerical value of  $a_{e^-}$  from potential-difference measurements vs. the SHE; hence, as for the value of  $E$  (V vs. the SHE), the numerical value of  $a_{e^-}$  depends on the SHE convention. Equilibrium constants may be written for these half cell reactions in the following way:

$$K^\circ (\text{II.25}) = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} \cdot a_{e^-}} \quad (\text{II.29})$$

$$K^\circ (\text{II.26}) = \frac{a_{\text{H}^+} \cdot a_{e^-}}{\sqrt{f_{\text{H}_2}}} = 1 \quad (\text{by definition}) \quad (\text{II.30})$$

In addition,  $\Delta_r G_m^\circ$  (II.26) = 0,  $\Delta_r H_m^\circ$  (II.26) = 0,  $\Delta_r S_m^\circ$  (II.26) = 0 by definition, at all temperatures, and therefore  $\Delta_r G_m^\circ$  (II.25) =  $\Delta_r G_m^\circ$  (II.24). From  $\Delta_r G_m^\circ$  (II.26) and the values given at 298.15 K in selected auxiliary data for  $H_2(g)$  and  $H^+$ , the corresponding values for  $e^-$  can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (II.24), if  $p_{H_2}$  and  $a_{H^+}$  are equal to unity (*cf.* Eq. (II.22)):

$$E(\text{II.24}) = E^\circ(\text{II.24}) - RT \ln \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \quad (\text{II.31})$$

For the standard hydrogen electrode  $a_{e^-} = 1$  (by the convention expressed in Eq. (II.30)), while rearrangement of Eq. (II.29) for the half cell containing the iron perchlorates in cell (II.23) gives:

$$-\log_{10} a_{e^-} = \log_{10} K^\circ(\text{II.25}) - \log_{10} \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)$$

and from Eq. (II.27):

$$-\log_{10} a_{e^-} = \log_{10} K^\circ(\text{II.24}) - \log_{10} \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \quad (\text{II.32})$$

and

$$-\log_{10} a_{e^-} = \frac{F}{RT \ln(10)} E(\text{II.24}) \quad (\text{II.33})$$

which is a specific case of the general equation (II.28).

The splitting of redox reactions into two half cell reactions by introducing the symbol “ $e^-$ ”, which according to Eq. (II.27) is related to the standard electrode potential, is arbitrary, but useful (this  $e^-$  notation does not in any way refer to solvated electrons). When calculating the equilibrium composition of a chemical system, both “ $e^-$ ”, and  $H^+$  can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc.* may be defined for both. However, while  $H^+$  represents the hydrated proton in aqueous solution, the above equations use only the activity of “ $e^-$ ”, and never the concentration of “ $e^-$ ”. Concentration to activity conversions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the “electron activity” of an aqueous solution with the symbol “pe” or “p $\mathcal{E}$ ” ( $= -\log_{10} a_{e^-}$ ) by analogy with pH ( $= -\log_{10} a_{H^+}$ ), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either “Eh” or “ $E_H$ ” (see for example [1981STU/MOR], [1982DRE], [1984HOS], [1986NOR/MUN]).

In this review, the symbol  $E^\circ$  is used to denote the so-called “formal potential” [1974PAR]. The formal (or “conditional”) potential can be regarded as a

standard potential for a particular medium in which the activity coefficients are independent (or approximately so) of the reactant concentrations [1985BAR/PAR] (the definition of  $E^{\circ}$  parallels that of “concentration quotients” for equilibria). Therefore, from

$$E = E^{\circ} - \frac{RT}{nF} \sum \nu_i \ln c_i \quad (\text{II.34})$$

$E^{\circ}$  is the potential  $E$  for a cell when the ratio of the *concentrations* (not the activities) on the right-hand side and the left-hand side of the cell reaction is equal to unity, and

$$E_c^{\circ} = E_c^{\circ} - \frac{RT}{nF} \sum \nu_i \ln \gamma_{c,i} \quad (\text{II.35a})$$

$$E_c^{\circ} = E_c^{\circ} - \frac{RT}{nF} \sum \nu_i \ln (\xi \cdot \gamma_{m,i} \cdot \rho_{\text{H}_2\text{O}}^*) \quad (\text{II.35b})$$

$$\gamma_{c,i} = \left( \frac{m_i/m^{\circ}}{c_i/c^{\circ}} \right) (\rho_{\text{H}_2\text{O}}^* / \rho^{\circ}) \gamma_{m,i} \quad (\text{II.35c})^1$$

where the  $\gamma_{c,i}$  and  $\gamma_{m,i}$  are the activity coefficients on amount concentration and molality basis, respectively [2008GAM/LOR], related by Eq. (II.35c),  $\rho_{\text{H}_2\text{O}}^*$  is the density of pure water, and  $\xi$  is  $(m_i/c_i)$ , the ratio of molality to molarity (*cf.* Section II.2). The medium must be specified. Equation (II.35c) has been derived most elegantly by [1959ROB/STO].

## II.1.8 pH

Because of the importance that potentiometric methods have in the determination of equilibrium constants in aqueous solutions, a short discussion on the definition of “pH” and a simplified description of the experimental techniques used to measure pH will be given here. For a comprehensive account, see [2002BUC/RON].

The acidity of aqueous solutions is often expressed in a logarithmic scale of the hydrogen ion activity. The definition of pH as:

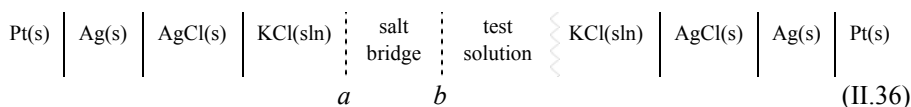
$$\text{pH} = -\log_{10} a_{\text{H}^+} = -\log_{10} (m_{\text{H}^+} \gamma_{\text{H}^+})$$

can only be strictly used in the range of the limiting Debye-Hückel equation (that is, in extremely dilute solutions). In practice the use of pH values requires extra assumptions as to the values for single ion activities. In this review values of pH are used to describe qualitatively the ranges of acidity of experimental studies, and the assumptions described in Appendix B are used to calculate single ion activity coefficients.

The determination of pH is often performed by potential-difference measurements of galvanic cells involving liquid junctions [1969ROS], [1973BAT]. A common

<sup>1</sup>  $\rho_{\text{H}_2\text{O}}^*$  is a variable depending on  $T$ ,  $m^{\circ} = 1 \text{ mol}\cdot\text{kg}^{-1}$ ,  $c^{\circ} = 1 \text{ mol}\cdot\text{dm}^{-3}$ .

setup is a cell made up of a reference half cell (e.g., Ag(s)|AgCl(s) in a solution of constant chloride concentration), a salt bridge, the test solution, and a glass electrode (which encloses a solution of constant acidity and an internal reference half cell):



where  $\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array}$  stands for a glass membrane (permeable to hydrogen ions).

The potential difference of such a cell is given by:

$$E = E^* - \frac{RT}{nF} \ln a_{\text{H}^+} + E_j$$

where  $E^*$  is a constant, and  $E_j$  is the liquid junction potential. The purpose of the salt bridge is to minimise the junction potential in junction “b”, while keeping constant the junction potential for junction “a”. Two methods are most often used to reduce and control the value of  $E_j$ . An electrolyte solution of *high* concentration (the “salt bridge”) is a requirement of both methods. In the first method, the salt bridge is a saturated (or nearly saturated) solution of potassium chloride. A problem with a bridge of high potassium concentration is that potassium perchlorate might precipitate<sup>1</sup> inside the liquid junction when the test solution contains a high concentration of perchlorate ions.

In the other method the salt bridge contains the same *high* concentration of the same inert electrolyte as the test solution (for example, 3 M NaClO<sub>4</sub>). However, if the concentration of the background electrolyte in the salt bridge and test solutions is reduced, the values of  $E_j$  are dramatically increased. For example, if both the bridge and the test solution have [ClO<sub>4</sub><sup>-</sup>] = 0.1 M as background electrolyte, the dependence of the liquid junction at “b” on acidity is  $E_j \approx -440 [\text{H}^+] \text{ mV} \cdot \text{dm}^3 \cdot \text{mol}^{-1}$  at 25 °C [1969ROS] (p.110), which corresponds to an error of  $\geq 0.07$  in pH at a pH value of 2.

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an “operational” definition of pH is given by IUPAC [1993MIL/CVI]. This definition involves the measurement of pH differences between the test solution and standard solutions of known pH and similar ionic strength (in this way similar values of  $\gamma_{\text{H}^+}$  and  $E_j$  cancel each other when potential-difference values are subtracted).

Another method of determining the molal H<sup>+</sup> concentration,  $\log_{10} m_{\text{H}^+}$ , in chloride solutions up to high ionic strength was proposed by Knauss *et al.* [1990KNA/WOL]. The activity of HCl ( $a_{\text{HCl}}$ ) can be measured with a liquid junction free cell consisting of a H<sup>+</sup> sensitive glass electrode and a chloride sensitive electrode from the relation:

$$\log_{10} a_{\text{HCl}} = \frac{1}{2} (\log_{10} m_{\text{H}^+} + \log_{10} m_{\text{Cl}^-} + \log_{10} \gamma_{\text{H}^+} + \log_{10} \gamma_{\text{Cl}^-}) \quad (\text{II.37})$$

<sup>1</sup> KClO<sub>4</sub>(cr) has a solubility of  $\approx 0.15$  M in pure water at 25 °C

The value of  $\log_{10} m_{\text{H}^+}$  in the test solution can then be derived from the measured value of  $\log_{10} a_{\text{HCl}}$ , the given chloride concentration  $\log_{10} m_{\text{Cl}^-}$  and the activity coefficients  $\log_{10} \gamma_{\text{H}^+}$  and  $\log_{10} \gamma_{\text{Cl}^-}$  which can be calculated either with the SIT or, for higher chloride concentrations, with the Pitzer equations as proposed by [1990KNA/WOL].

The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and other equilibria, it is necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known, or constant. Only in this manner is it possible to use the mass balance equations for the various components together with the measurement of one or more free concentrations to obtain the information desired [1961ROS/ROS], [1990BEC/NAG], [1997ALL/BAN], pp. 326–327. For equilibria involving hydrogen ions, it is necessary to use concentration units, rather than hydrogen ion activity. For experiments in an ionic medium, where the concentration of an “inert” electrolyte is much larger than the concentration of reactants and products we can ensure that, as a first approximation, their trace activity coefficients remain constant even for moderate variations of the corresponding total concentrations. Under these conditions of fixed ionic strength the free proton concentration may be measured directly, thereby defining it in terms of  $-\log_{10} [\text{H}^+]$  (also often referred to as  $\text{pH}_c$ , and correspondingly  $\text{pH}_m$  for  $\log_{10} m_{\text{H}^+}$ ) rather than on the activity scale as pH, and the value of  $-\log_{10} [\text{H}^+]$  and pH will differ by a constant term, *i.e.*,  $\log_{10} \gamma_{\text{H}^+}$ . Equilibrium constants deduced from measurements in such ionic media are therefore *conditional* constants, because they refer to the given medium, not to the standard state. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed electrolyte systems to a *common* standard state. Such procedures are discussed in Appendix B.

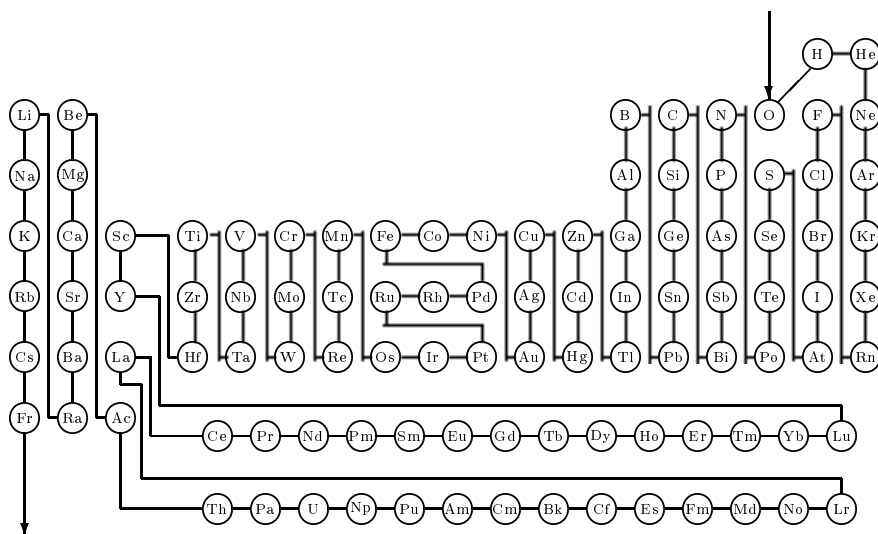
Note that the precision of the measurement of  $-\log_{10} [\text{H}^+]$  and pH is virtually the same, in very good experiments,  $\pm 0.001$ . However, the accuracy is generally considerably poorer, depending in the case of glass electrodes largely on the response of the electrode (linearity, age, pH range, *etc.*), and to a lesser extent on the calibration method employed, although the stoichiometric  $-\log_{10} [\text{H}^+]$  calibration standards can be prepared far more accurately than the commercial pH standards.

### II.1.9 Order of formulae

To be consistent with CODATA, the data tables are given in “*Standard Order of Arrangement*” [1982WAG/EVA]. This scheme is presented in Figure II-1 below, and shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*,  $U^{4+}$ ), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing coefficients of the lower rank elements. For example, in the U–O–F class of compounds and complexes, a typical sequence would be  $UOF_2(\text{cr})$ ,  $UOF_4(\text{cr})$ ,  $UOF_4(\text{g})$ ,  $UO_2F(\text{aq})$ ,  $UO_2F^+$ ,  $UO_2F_2(\text{aq})$ ,  $UO_2F_2(\text{cr})$ ,  $UO_2F_2(\text{g})$ ,  $UO_2F_3^-$ ,  $UO_2F_4^{2-}$ ,  $U_2O_3F_6(\text{cr})$ , *etc.* [1992GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

Figure II-1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from [1982WAG/EVA]).



### II.1.10 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [1987GAR/PAR]. A reference code is made up of the four digits of the year of appearance, followed by the first three letters of the surnames of the first two authors, separated by a slash.

If there are multiple reference codes, a “2” will be added to the second one, a “3” to the third one, and so forth. Reference codes are always enclosed in square brackets.

## II.2 Units and conversion factors

Thermodynamic data are given according to the *Système International d'unités* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non-thermodynamic units, are given in Table II-4.

Table II-4: Unit conversion factors.

To convert from (non-SI unit symbol)	to (SI unit symbol)	multiply by
ångström (Å)	metre (m)	$1 \times 10^{-10}$ (exactly)
standard atmosphere (atm)	pascal (Pa)	$1.01325 \times 10^5$ (exactly)
bar (bar)	pascal (Pa)	$1 \times 10^5$ (exactly)
thermochemical calorie (cal)	joule (J)	4.184 (exactly)
entropy unit e.u. $\hat{=}$ cal·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	4.184 (exactly)

Since a large part of the NEA TDB Project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses “M” as an abbreviation of “mol·dm<sup>-3</sup>” for molarity,  $c$ , and, in Appendices B and C, “m” as an abbreviation of “mol·kg<sup>-1</sup>” for molality,  $m$ . It is often necessary to convert data from molarity to molality and *vice versa*. This conversion is used for the correction and extrapolation of equilibrium data to zero ionic strength by the specific ion interaction treatment, which works on molality basis (*cf.* Appendix B). This conversion is made in the following way.

Molality<sup>1</sup>,  $m_B$ , is defined as the amount of substance,  $n_B$  dissolved in the mass of pure solvent,  $m_A$ , which in most cases is pure water

$$m_B = n_B / m_A.$$

Molarity (concentration),  $c_B$ , is defined as the amount of substance,  $n_B$ , dissolved in the volume,  $V$ , of solution

$$c_B = n_B / V.$$

Density of solution,  $\rho$ , is given by mass of solution divided by its volume,

$$\rho = (n_B M_B + m_A) / V$$

where  $M$  is the molar mass of the solute.

<sup>1</sup> In this derivation the symbol  $m$  is used with two different meanings:  $m_B$  denotes the *molality* of solute B and  $m_A$  denotes the *mass* of solvent A.

From this it follows that:

$$m_B = \frac{c_B}{\rho - c_B M_B}$$

When the ionic strength is kept high and constant by an inert electrolyte, I, the ratio  $m_B/c_B$  can be approximated by

$$\frac{m_B}{c_B} = \frac{1}{\rho - c_1 M_1}$$

where  $c_1$  is the concentration of the inert electrolyte and  $M_1$  its molar mass.

Baes and Mesmer [1976BAE/MES], (p.439) give a table with conversion factors (from molarity to molality) for nine electrolytes at various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnel and Novotný [1985SOH/NOV], are reported in Table II-5.

Example:

$$1.00 \text{ M NaClO}_4 \hat{=} 1.05 \text{ m NaClO}_4$$

$$1.00 \text{ M NaCl} \hat{=} 1.02 \text{ m NaCl}$$

$$4.00 \text{ M NaClO}_4 \hat{=} 4.95 \text{ m NaClO}_4$$

$$6.00 \text{ M NaNO}_3 \hat{=} 7.55 \text{ m NaNO}_3$$

It should be noted that equilibrium constants need also to be converted if the concentration scale is changed from molarity to molality or *vice versa*. For a general equilibrium reaction,  $0 = \sum_B \nu_B B$ , the equilibrium constants can be expressed either in molarity or molality units,  $K_c$  or  $K_m$ , respectively:

$$\log_{10} K_c = \sum_B \nu_B \log_{10} c_B$$

$$\log_{10} K_m = \sum_B \nu_B \log_{10} m_B$$

With  $(m_B/c_B) = \xi$ , or  $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \xi$ , the relationship between  $K_c$  and  $K_m$  becomes very simple, as shown in Eq. (II.38).

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \xi \quad (\text{II.38})$$

$\sum_B \nu_B$  is the sum of the stoichiometric coefficients of the solutes, *cf.* Eq. (II.55) and the values of  $\xi$  are the factors for the conversion of molarity to molality as tabulated in Table II-5 for several electrolyte media at 298.15 K. The differences between the values in Table II-5 and the values listed in the uranium NEA TDB review [1992GRE/FUG] (p.23) are found at the highest concentrations, and are no larger than  $\pm 0.003 \text{ dm}^3 \cdot \text{kg}^{-1}$ , reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq. (II.38) in the values of  $\log_{10} K_m$  will be no larger than  $\pm 0.001 \sum_B \nu_B$ .



Table II-5: Factors  $\xi$  for the conversion of molarity,  $c_B$ , to molality,  $m_B$ , of a substance B, in various media at 298.15 K (calculated from densities in [1985SOH/NOV]).

$c$ (M)	$\xi = m_B / c_B$ (dm <sup>3</sup> of solution per kg of H <sub>2</sub> O)							
	HClO <sub>4</sub>	NaClO <sub>4</sub>	LiClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	Ba(ClO <sub>4</sub> ) <sub>2</sub>	HCl	NaCl	LiCl
0.10	1.0077	1.0075	1.0074	1.0091	1.0108	1.0048	1.0046	1.0049
0.25	1.0147	1.0145	1.0141	1.0186	1.0231	1.0076	1.0072	1.0078
0.50	1.0266	1.0265	1.0256	1.0351	1.0450	1.0123	1.0118	1.0127
0.75	1.0386	1.0388	1.0374	1.0523	1.0685	1.0172	1.0165	1.0177
1.00	1.0508	1.0515	1.0496	1.0703	1.0936	1.0222	1.0215	1.0228
1.50	1.0759	1.0780	1.0750	1.1086	1.1491	1.0324	1.0319	1.0333
2.00	1.1019	1.1062	1.1019		1.2125	1.0430	1.0429	1.0441
3.00	1.1571	1.1678	1.1605		1.3689	1.0654	1.0668	1.0666
4.00	1.2171	1.2374	1.2264			1.0893	1.0930	1.0904
5.00	1.2826	1.3167				1.1147	1.1218	1.1156
6.00	1.3547	1.4077				1.1418		1.1423
$c$ (M)	KCl	NH <sub>4</sub> Cl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaBr	HNO <sub>3</sub>	NaNO <sub>3</sub>	LiNO <sub>3</sub>
0.10	1.0057	1.0066	1.0049	1.0044	1.0054	1.0056	1.0058	1.0059
0.25	1.0099	1.0123	1.0080	1.0069	1.0090	1.0097	1.0102	1.0103
0.50	1.0172	1.0219	1.0135	1.0119	1.0154	1.0169	1.0177	1.0178
0.75	1.0248	1.0318	1.0195	1.0176	1.0220	1.0242	1.0256	1.0256
1.00	1.0326	1.0420	1.0258	1.0239	1.0287	1.0319	1.0338	1.0335
1.50	1.0489	1.0632	1.0393	1.0382	1.0428	1.0478	1.0510	1.0497
2.00	1.0662	1.0855	1.0540	1.0546	1.0576	1.0647	1.0692	1.0667
3.00	1.1037	1.1339	1.0867	1.0934	1.0893	1.1012	1.1090	1.1028
4.00	1.1453	1.1877	1.1241	1.1406	1.1240	1.1417	1.1534	1.1420
5.00		1.2477		1.1974	1.1619	1.1865	1.2030	1.1846
6.00					1.2033	1.2361	1.2585	1.2309
$c$ (M)	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	NaSCN
0.10	1.0077	1.0064	1.0044	1.0082	1.0074	1.0027	1.0042	1.0069
0.25	1.0151	1.0116	1.0071	1.0166	1.0143	1.0030	1.0068	1.0130
0.50	1.0276	1.0209	1.0127	1.0319	1.0261	1.0043	1.0121	1.0234
0.75	1.0405	1.0305	1.0194	1.0486	1.0383	1.0065	1.0185	1.0342
1.00	1.0539	1.0406	1.0268	1.0665	1.0509	1.0094	1.0259	1.0453
1.50	1.0818	1.0619	1.0441	1.1062	1.0773	1.0170	1.0430	1.0686
2.00	1.1116	1.0848		1.1514	1.1055	1.0268	1.0632	1.0934
3.00	1.1769	1.1355		1.2610	1.1675		1.1130	1.1474
4.00	1.2512	1.1935		1.4037	1.2383		1.1764	1.2083
5.00	1.3365	1.2600			1.3194		1.2560	1.2773
6.00	1.4351	1.3365			1.4131			1.3557

## II.3 Standard and reference conditions

### II.3.1 Standard state

A precise definition of the term “standard state” has been given by IUPAC [1982LAF]. The fact that only changes in thermodynamic parameters, but not their absolute values, can be determined experimentally, makes it important to have a well-defined standard state that forms a base line to which the effect of variations can be referred. The IUPAC [1982LAF] definition of the standard state has been adopted in the NEA TDB Project. The standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  (1 bar), has therefore also been adopted, *cf.* Section II.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section II.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.
- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.
- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.
- The standard state for a solute B in a solution is the (hypothetical) state of solute at the standard molality  $m^\circ$ , standard pressure  $p^\circ$  or standard concentration  $c^\circ$  and exhibiting infinitely dilute solution behaviour.

It should be emphasised that the use of superscript,  $^\circ$ , *e.g.*, in  $\Delta_r H_m^\circ$ , implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section II.3.3) are listed in Table II-6.

Table II-6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [1982WAG/EVA], [1989COX/WAG], [1991DIN], [2005GAM/BUG], [2005OLI/NOL].

O <sub>2</sub>	gaseous	Zn	crystalline, hexagonal
H <sub>2</sub>	gaseous	Cd	crystalline, hexagonal
He	gaseous	Hg	liquid
Ne	gaseous	Cu	crystalline, cubic
Ar	gaseous	Ag	crystalline, cubic
Kr	gaseous	Ni	crystalline, fcc
Xe	gaseous	Fe	crystalline, cubic, bcc
F <sub>2</sub>	gaseous	Tc	crystalline, hexagonal
Cl <sub>2</sub>	gaseous	V	crystalline, cubic
Br <sub>2</sub>	liquid	Ti	crystalline, hexagonal
I <sub>2</sub>	crystalline, orthorhombic	Am	crystalline, dhcp
S	crystalline, orthorhombic	Pu	crystalline, monoclinic
Se	crystalline, trigonal	Np	crystalline, orthorhombic
Te	crystalline, hexagonal	U	crystalline, orthorhombic
N <sub>2</sub>	gaseous	Th	crystalline, cubic
P	crystalline, cubic (“white”)	Be	crystalline, hexagonal
As	crystalline, rhombohedral (“grey”)	Mg	crystalline, hexagonal
Sb	crystalline, rhombohedral	Ca	crystalline, cubic, fcc
Bi	crystalline, rhombohedral	Sr	crystalline, cubic, fcc
C	crystalline, hexagonal (graphite)	Ba	crystalline, cubic
Si	crystalline, cubic	Li	crystalline, cubic
Ge	crystalline, cubic	Na	crystalline, cubic
Sn	crystalline, tetragonal (“white”)	K	crystalline, cubic
Pb	crystalline, cubic	Rb	crystalline, cubic
B	crystalline, rhombohedral	Cs	crystalline, cubic
Al	crystalline, cubic		

### II.3.2 Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by IUPAC [1982LAF].

However, the majority of the thermodynamic data published in the scientific literature, and used for the evaluations in this review, refers to the old standard state pressure of 1 “standard atmosphere” (= 0.101325 MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propa-

gation of errors. In practice the parameters affected by the change between these two standard state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [1982WAG/EVA], see also Freeman [1984FRE].

The following expressions define the effect of pressure on the properties of all substances:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1 - \alpha T) \quad (\text{II.39})$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (\text{II.40})$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \quad (\text{II.41})$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (\text{II.42})$$

$$\text{where } \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad (\text{II.43})$$

For ideal gases,  $V = RT/p$  and  $\alpha = R/pV = 1/T$ . The conversion equations listed below (Eqs. (II.44) to (II.51)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript <sup>(atm)</sup>, and those that refer to the new standard state pressure of 1 bar are assigned the superscript <sup>(bar)</sup>.

For all substances the changes in the enthalpy of formation and heat capacity are much smaller than the experimental accuracy and can be disregarded. This is exactly true for ideal gases.

$$\Delta_f H^{(\text{bar})}(T) - \Delta_f H^{(\text{atm})}(T) = 0 \quad (\text{II.44})$$

$$C_p^{(\text{bar})}(T) - C_p^{(\text{atm})}(T) = 0 \quad (\text{II.45})$$

For gaseous substances, the entropy difference is:

$$\begin{aligned} S^{(\text{bar})}(T) - S^{(\text{atm})}(T) &= R \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) = R \ln 1.01325 \\ &= 0.1094 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned} \quad (\text{II.46})$$

This is exactly true for ideal gases, as follows from Eq. (II.41) with  $\alpha = R/pV$ . The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\begin{aligned}\Delta_r S^{(\text{bar})} - \Delta_r S^{(\text{atm})} &= \delta R \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= 0.1094 \delta \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}\quad (\text{II.47})$$

where  $\delta$  is the net increase in moles of gas in the process.

Similarly, the change in the Gibbs energy of a process between the two standard state pressures is:

$$\begin{aligned}\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})} &= -\delta RT \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= -0.03263 \delta \text{ kJ} \cdot \text{mol}^{-1} \text{ at } 298.15 \text{ K.}\end{aligned}\quad (\text{II.48})$$

Eq. (II.48) applies also to  $\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})}$ , since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})} = -0.03263 \delta \text{ kJ} \cdot \text{mol}^{-1} \text{ at } 298.15 \text{ K.} \quad (\text{II.49}).$$

The changes in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq. (II.48),

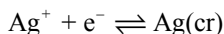
$$\begin{aligned}\log_{10} K^{(\text{bar})} - \log_{10} K^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{RT \ln 10} \\ &= \delta \frac{\ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{\ln 10} = \delta \log_{10} \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= 0.005717 \delta\end{aligned}\quad (\text{II.50})$$

$$\begin{aligned}E^{(\text{bar})} - E^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{nF} \\ &= \delta \frac{RT \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{nF} \\ &= \delta \frac{0.0003382}{n} \text{ V at } 298.15 \text{ K}\end{aligned}\quad (\text{II.51})$$

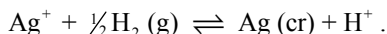
It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.



This definition will not be changed, although a gaseous substance,  $\text{H}_2(\text{g})$ , is involved in the process. The change in the potential with pressure for an electrode potential conventionally written as:

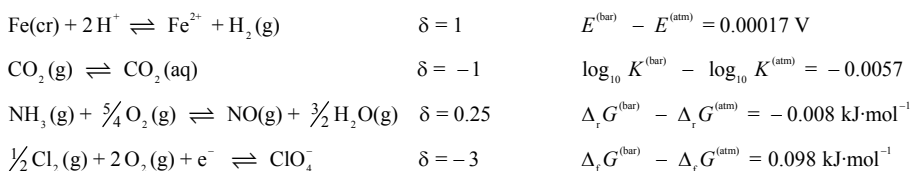


should thus be calculated from the balanced reaction that includes the hydrogen electrode,



Here  $\delta = -0.5$ . Hence, the contribution to  $\delta$  from an electron in a half cell reaction is the same as the contribution of a gas molecule with the stoichiometric coefficient of 0.5. This leads to the same value of  $\delta$  as the combination with the hydrogen half cell.

Example:



### II.3.3 Reference temperature

The definitions of standard states given in Section II.3 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [1982LAF], the reference temperature chosen in the NEA TDB Project is  $T = 298.15 \text{ K}$  or  $t = 25.00 \text{ }^\circ\text{C}$ . Where necessary for the discussion, values of experimentally measured temperatures are reported after conversion to the IPTS-68 [1969COM]. The relation between the absolute temperature  $T$  (K, kelvin) and the Celsius temperature  $t$  ( $^\circ\text{C}$ ) is defined by  $t / ^\circ\text{C} = T / \text{K} - 273.15$ .

## II.4 Fundamental physical constants

To ensure the consistency with other NEA TDB Reviews, the fundamental physical constants are taken from a publication by CODATA [1986COD]. Those relevant to this review are listed in Table II-7. Updated values of the fundamental constants can be obtained from CODATA, notably through its Internet site. In most cases, recalculation of the NEA TDB database entries with the updated values of the fundamental constants will not introduce significant (with respect to their quoted uncertainties) excursions from the current NEA TDB selections.

Table II-7: Fundamental physical constants. These values have been taken from CODATA [1986COD]. The digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

Quantity	Symbol	Value	Units
speed of light in vacuum	$c_0$	299 792 458	$\text{m}\cdot\text{s}^{-1}$
permeability of vacuum	$\mu_0$	$4\pi\times 10^{-7} = 12.566\ 370\ 614\dots$	$10^{-7}\ \text{N}\cdot\text{A}^{-2}$
permittivity of vacuum	$\epsilon_0$	$1/\mu_0\ c^2 = 8.854\ 187\ 817\dots$	$10^{-12}\ \text{C}^2\cdot\text{J}^{-1}\cdot\text{m}^{-1}$
Planck constant	$h$	6.626 0755(40)	$10^{-34}\ \text{J}\cdot\text{s}$
elementary charge	$e$	1.602 177 33(49)	$10^{-19}\ \text{C}$
Avogadro constant	$N_A$	6.022 1367(36)	$10^{23}\ \text{mol}^{-1}$
Faraday constant	$F$	96 485.309(29)	$\text{C}\cdot\text{mol}^{-1}$
molar gas constant	$R$	8.314 510(70)	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Boltzmann constant, $R/N_A$	$k_B$	1.380 658(12)	$10^{-23}\ \text{J}\cdot\text{K}^{-1}$
Non-SI units used with SI:			
electronvolt, (e/C) J	eV	1.602 177 33(49)	$10^{-19}\ \text{J}$
atomic mass unit,	u	1.660 5402(10)	$10^{-27}\ \text{kg}$
$1\ \text{u} = m_u = \frac{1}{12}\ m(^{12}\text{C})$			

## II.5 Uncertainty estimates

One of the principal objectives of the NEA TDB development effort is to provide an idea of the uncertainties associated with the data selected in the reviews. In general the uncertainties should define the range within which the corresponding data can be reproduced with a probability of 95%. In many cases, a full statistical treatment is limited or impossible due to the availability of only one or a few data points. Appendix C describes in detail the procedures used for the assignment and treatment of uncertainties, as well as the propagation of errors and the standard rules for rounding.

## II.6 The NEA TDB system

A database system has been developed at the NEA Data Bank that allows the storage of thermodynamic parameters for individual species as well as for reactions. The structure of the database system allows consistent derivation of thermodynamic data for individual species from reaction data at standard conditions, as well as internal recalculations of data at standard conditions. If a selected value is changed, all the dependent values will be recalculated consistently. The maintenance of consistency of all the selected data, including their uncertainties (*cf.* Appendix C), is ensured by the software developed for this purpose at the NEA Data Bank. The literature sources of the data are also stored in the database.

The following thermodynamic parameters, valid at the reference temperature of 298.15 K and at the standard pressure of 1 bar, are stored in the database:

$\Delta_f G_m^\circ$	the standard molar Gibbs energy of formation from the elements in their reference state ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta_f H_m^\circ$	the standard molar enthalpy of formation from the elements in their reference state ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$S_m^\circ$	the standard molar entropy ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$C_{p,m}^\circ$	the standard molar heat capacity ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) at constant pressure.

For aqueous neutral species and ions, the values of  $\Delta_f G_m^\circ$ ,  $\Delta_f H_m^\circ$ ,  $S_m^\circ$  and  $C_{p,m}^\circ$  correspond to the standard partial molar quantities, and for individual aqueous ions they are relative quantities, defined with respect to the aqueous hydrogen ion, according to the convention [1989COX/WAG] that  $\Delta_f H_m^\circ(\text{H}^+, T) = 0$  and that  $S_m^\circ(\text{H}^+, T) = 0$ . Furthermore, for an *ionised solute* B containing any number of different cations and anions:

$$\begin{aligned}\Delta_f H_m^\circ(\text{B}_\pm, \text{aq}) &= \sum_+ \nu_+ \Delta_f H_m^\circ(\text{cation}, \text{aq}) + \sum_- \nu_- \Delta_f H_m^\circ(\text{anion}, \text{aq}) \\ S_m^\circ(\text{B}_\pm, \text{aq}) &= \sum_+ \nu_+ S_m^\circ(\text{cation}, \text{aq}) + \sum_- \nu_- S_m^\circ(\text{anion}, \text{aq})\end{aligned}$$

As the thermodynamic parameters vary as a function of temperature, provision is made for including the compilation of the coefficients of empirical temperature functions for these data, as well as the temperature ranges over which they are valid. In many cases the thermodynamic data measured or calculated at several temperatures were published for a particular species, rather than the deduced temperature functions. In these cases, a linear regression method is used in this review to obtain the most significant coefficients of the following empirical function for a thermodynamic parameter,  $X$ :

$$\begin{aligned}X(T) &= a_x + b_x T + c_x T^2 + d_x T^{-1} + e_x T^{-2} + f_x \ln T + g_x T \ln T \\ &+ h_x \sqrt{T} + \frac{i_x}{\sqrt{T}} + j_x T^3 + k_x T^{-3}.\end{aligned}\quad (\text{II.53})$$

Most temperature variations can be described with three or four parameters. In the present series, only  $C_{p,m}(T)$ , *i.e.*, the thermal functions of the heat capacities of individual species are considered and stored in the database. They refer to the relation:

$$C_{p,m}^\circ(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + fT^3 \quad (\text{II.54})$$

(where the subindices for the coefficients have been dropped) and are listed in the selected value tables.

The pressure dependence of thermodynamic data has not been the subject of critical analysis in the present compilation. The reader interested in higher temperatures and pressures, or the pressure dependency of thermodynamic functions for geochemical applications, is referred to the specialised literature in this area, *e.g.*, [1982HAM],



[1984MAR/MES], [1988SHO/HEL], [1988TAN/HEL], [1989SHO/HEL], [1989SHO/HEL2], [1990MON], [1991AND/CAS].

Selected standard thermodynamic data referring to chemical reactions are also compiled in the database. A chemical reaction “r”, involving reactants and products “B”, can be abbreviated as:

$$0 = \sum_B \nu_B B \quad (\text{II.55})$$

where the stoichiometric coefficients  $\nu_B$  are positive for products, and negative for reactants. The reaction parameters considered in the NEA TDB system include:

$\log_{10} K_r^\circ$	the equilibrium constant of the reaction, logarithmic
$\Delta_r G_m^\circ$	the molar Gibbs energy of reaction ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta_r H_m^\circ$	the molar enthalpy of reaction ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta_r S_m^\circ$	the molar entropy of reaction ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$\Delta_r C_{p,m}^\circ$	the molar heat capacity of reaction ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) at constant pressure.

The temperature functions of these data, if available, are stored according to Eq. (II.53).

The equilibrium constant,  $K_r^\circ$ , is related to  $\Delta_r G_m^\circ$  according to the following relation:

$$\log_{10} K_r^\circ = -\frac{\Delta_r G_m^\circ}{RT \ln(10)}$$

and can be calculated from the individual values of  $\Delta_r G_m^\circ(B)$  (for example, those given in selected values tables), according to:

$$\log_{10} K_r^\circ = -\frac{1}{RT \ln(10)} \sum_B \nu_B \Delta_r G_m^\circ(B) \quad (\text{II.56})$$

## II.7 Presentation of the selected data

The selected data are presented in Chapters III and IV. Unless otherwise indicated, they refer to standard conditions (*cf.* Section II.3) and 298.15 K (25 °C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix C).

Chapters III contains a table of selected thermodynamic data for individual compounds and complexes of tin (Table III-1), a table of selected reaction data (Table III-2) for reactions concerning tin species and a table containing the heat capacities of individual species of tin (Table III-3) that have been used in the evaluations. The selection of all these data is discussed in Chapters V to XI.

Chapter IV contains tables of thermodynamic data for individual species (Table IV-1) and reaction data (Table IV-2), for auxiliary compounds and complexes that do not contain iron. Most of these values are the CODATA Key Values [1989COX/WAG]. The selection of the remaining auxiliary data is discussed in [1992GRE/FUG], [1999RAR/RAN], [2001LEM/FUG], [2005GAM/BUG], [2005OLI/NOL] and [2008RAN/FUG].

All the selected data presented in Table III-1, Table III-2, Table III-3, Table IV-1 and Table IV-2 are internally consistent. This consistency is maintained by the internal consistency verification and recalculation software developed at the NEA Data Bank in conjunction with the NEA TDB database system, *cf.* Section II.6. Therefore, when using the selected data, the auxiliary data of Chapter IV must be used together with the data in Chapter III to ensure internal consistency of the data set.

It is important to note that Table III-2 and Table IV-2 include only those species for which the primary selected data are reaction data. The formation data derived therefrom and listed in Table III-1 are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in Table III-2 and Table IV-2, rather than taking the derived values in Table III-1 and Table IV-1 to calculate the reaction data with Eq. (II.56). The latter approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00 °C), but they can be recalculated to other temperatures if the corresponding data (enthalpies, entropies, heat capacities) are available [1997PUI/RAR]. For example, the temperature dependence of the standard reaction Gibbs energy as a function of the standard reaction entropy at the reference temperature ( $T_0 = 298.15$  K), and of the heat capacity function is:

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T_0) + \int_{T_0}^T \Delta_r C_{p,m}^\circ(T) dT - T \left( \Delta_r S_m^\circ(T_0) + \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ(T)}{T} dT \right),$$

and the temperature dependence of the standard equilibrium constant as a function of the standard reaction enthalpy and heat capacity is:

$$\begin{aligned} \log_{10} K^\circ(T) = & \log_{10} K^\circ(T_0) - \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left( \frac{1}{T} - \frac{1}{T_0} \right) \\ & - \frac{1}{RT \ln(10)} \int_{T_0}^T \Delta_r C_{p,m}^\circ(T) dT + \frac{1}{R \ln(10)} \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ(T)}{T} dT, \end{aligned}$$

where  $R$  is the gas constant (*cf.* Table II-7).

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150 °C, with an additional uncertainty of perhaps about  $\pm 1$  to  $\pm 2$  in  $\log_{10} K$ , due to neglect of the heat-capacity contributions to the temperature correction. For isocoulombic/isoelectric reactions the uncertainty may be smaller; for a detailed discussion see [1997PUI/RAR]. However, it is important to observe that “new” aqueous species, *i.e.*, species not present in significant amounts at 298.15 K and therefore not detected, may be significant at higher temperatures, see for example the work by Ciavatta *et al.* [1987CIA/IUL]. Additional high-temperature experiments may therefore be needed in order to ascertain that proper chemical models are used in the modelling of hydrothermal systems. For many species, experimental thermodynamic data are not available to allow a selection of parameters describing the temperature dependence of equilibrium constants and Gibbs energies of formation. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [1997PUI/RAR]. The thermodynamic data in the selected set refer to infinite dilution for soluble species. Extrapolation of an equilibrium constant  $K$ , usually measured at high ionic strength, to  $K^\circ$  at  $I = 0$  using activity coefficients  $\gamma$ , is explained in Appendix B. The corresponding Gibbs energy of dilution is:

$$\Delta_{\text{dil}}G_{\text{m}} = \Delta_{\text{r}}G_{\text{m}}^{\circ} - \Delta_{\text{r}}G_{\text{m}} \quad (\text{II.57})$$

$$= -RT \Delta_{\text{r}} \ln \gamma_{\pm} \quad (\text{II.58})$$

Similarly  $\Delta_{\text{dil}}S_{\text{m}}$  can be calculated from  $\ln \gamma_{\pm}$  and its variations with  $T$ , while:

$$\Delta_{\text{dil}}H_{\text{m}} = RT^2 \frac{\partial}{\partial T} (\Delta_{\text{r}} \ln \gamma_{\pm})_p \quad (\text{II.59})$$

depends only on the variation of  $\gamma$  with  $T$ , which is neglected in this review, when no data on the temperature dependence of  $\gamma$ s are available. In this case the Gibbs energy of dilution  $\Delta_{\text{dil}}G_{\text{m}}$  is entirely assigned to the entropy difference. This entropy of reaction is calculated using  $\Delta_{\text{r}}G_{\text{m}}^{\circ} = \Delta_{\text{r}}H_{\text{m}}^{\circ} - T\Delta_{\text{r}}S_{\text{m}}^{\circ}$ , the value of  $\Delta_{\text{dil}}G_{\text{m}}$  and with the approximation that  $\Delta_{\text{dil}}H_{\text{m}} = 0$ .



## **Part 2**

### **Tables of selected data**



# Chapter III

## Selected tin data

This chapter presents the chemical thermodynamic data set for tin species that has been selected in this review. Table III-1 contains the recommended thermodynamic data of the tin compounds and species, Table III-2 the recommended thermodynamic data of chemical equilibrium reactions by which the tin compounds and complexes are formed, and Table III-3 the temperature coefficients from the available heat capacity data for species listed in Table III-1.

The species and reactions in the tables appear in standard order of arrangement. Table III-2 contains information only on those reactions for which primary data selections are made in Chapters V to XI of this review. These selected reaction data are used, together with data for key tin species and auxiliary data selected in this review, to derive the corresponding formation data in Table III-1. The uncertainties associated with values for key tin species and the auxiliary data are in some cases substantial, leading to comparatively large uncertainties in the formation quantities derived in this manner.

The values of  $\Delta_r G_m^\circ$  for many reactions are known more accurately than would be calculated directly from the uncertainties of the  $\Delta_f G_m^\circ$  values in Table III-1 and auxiliary data. The inclusion of a table for reaction data (Table III-2) in this report allows the use of equilibrium constants with total uncertainties that are based directly on the experimental accuracies. This is the main reason for including both Table III-1 and Table III-2.

The selected thermal functions of the heat capacities, listed in Table III-3 refer to the relation

$$C_{p,m}^\circ(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + fT^3$$

A detailed discussion of the selection procedure is presented in Chapters V to XI. It may be noted that this chapter contains data on more species or compounds than are present in the tables of Chapter III. The main reasons for this situation are the lack of information for a proper extrapolation of the primary data to standard conditions in some systems and lack of solid primary data in others.

A warning: The addition of any aqueous species and their data to this internally consistent data base can result in a modified data set, which is no longer rigorous and can lead to erroneous results. The situation is similar when gases or solids are added.

Table III-1: Selected thermodynamic data for tin compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapters V to XI. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$S_m^\circ$	$C_{p,m}^\circ$
	(kJ·mol <sup>-1</sup> )	(kJ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )
$\alpha$ -Sn	0.119 <sup>(a)</sup> ±0.162	-1.980 ±0.100	44.140 ±0.420	25.800 ±0.300
$\beta$ -Sn	0.000	0.000	51.180 ±0.080	27.110 ±0.080
Sn <sup>2+</sup>	-27.390 ±0.300	-9.617 ±1.236	-19.889 ±4.266	
Sn <sup>4+</sup>	46.711 <sup>(b)</sup> ±3.871			
SnH <sub>4</sub> (g)	188.065 <sup>(a)</sup> ±2.183	162.800 ±2.100	227.800 ±2.000	50.316 ±0.300
SnO(cr)	-255.446 <sup>(a)</sup> ±0.763	-284.240 ±0.760	57.180 ±0.220	47.760 ±0.080
SnO <sub>2</sub> (am)	-511.870 ±0.803			
SnO <sub>2</sub> (cass)	-516.640 <sup>(a)</sup> ±0.206	-577.630 ±0.200	51.770 ±0.140	55.260 ±0.090
SnOH <sup>+</sup>	-244.381 <sup>(b)</sup> ±2.303			
Sn <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	-998.766 <sup>(b)</sup> ±2.834			
Sn(OH) <sub>2</sub> (aq)	-457.833 <sup>(b)</sup> ±2.304			
Sn(OH) <sub>3</sub> <sup>-</sup>	-644.992 <sup>(b)</sup> ±3.440			
Sn(OH) <sub>4</sub> (aq)	-944.914 <sup>(b)</sup> ±0.666			

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Table III-1 (Continued)

Compound	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Sn(OH) <sub>5</sub> <sup>-</sup>	- 1132.965 <sup>(b)</sup> ±2.379			
Sn(OH) <sub>6</sub> <sup>2-</sup>	- 1312.625 <sup>(b)</sup> ±1.839			
SnF <sup>+</sup>	- 338.880 <sup>(b)</sup> ±1.321			
SnF <sub>2</sub> (aq)	- 641.181 <sup>(b)</sup> ±1.856			
SnF <sub>2</sub> (cr)		- 700.260 ±2.169		
SnF <sub>2</sub> (g)	- 543.387 <sup>(a)</sup> ±3.000	- 535.000 <sup>(b)</sup> ±3.000	282.100 ±0.100	49.700 ±0.100
SnF <sub>3</sub> <sup>-</sup>	- 937.602 <sup>(b)</sup> ±6.082			
BaSnF <sub>4</sub> (cr)			205.100 ±0.300	146.500 ±1.600
PbSnF <sub>4</sub> (cr)			223.700 ±0.300	162.400 ±0.800
SrSnF <sub>4</sub> (cr)			187.200 ±0.300	147.400 ±7.600
SnCl <sup>+</sup>	- 167.284 <sup>(b)</sup> ±1.186	- 163.997 <sup>(b)</sup> ±2.613	108.407 <sup>(b)</sup> ±9.613	
SnCl <sub>2</sub> (aq)	- 302.211 <sup>(b)</sup> ±1.042	- 324.077 <sup>(b)</sup> ±4.671	200.929 <sup>(b)</sup> ±16.023	
SnCl <sub>2</sub> (cr)	- 286.069 <sup>(a)</sup> ±2.206	- 327.900 ±2.200	133.960 ±0.530	77.960 ±0.310
SnCl <sub>2</sub> (g)	- 206.933 <sup>(a)</sup> ±4.300	- 197.500 <sup>(b)</sup> ±4.300	305.900 ±0.100	54.600 ±0.100
SnCl <sub>2</sub> · 2 H <sub>2</sub> O(cr)	- 760.532 <sup>(a)</sup> ±1.489	- 918.260 ±1.420	211.750 ±1.500	166.400 ±0.500
SnCl <sub>3</sub> <sup>-</sup>	- 433.212 <sup>(b)</sup> ±1.178			
SnCl <sub>4</sub> (g)	- 439.609 <sup>(a)</sup> ±3.500	- 478.500 <sup>(b)</sup> ±3.500	366.900 ±0.100	98.400 ±0.100
SnCl <sub>4</sub> (l)		- 517.000 ±2.000		

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Table III-1 (Continued)

Compound	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
SnCl <sub>4</sub> <sup>2-</sup>	- 563.847 <sup>(b)</sup> ±2.350			
Sn <sub>21</sub> Cl <sub>16</sub> (OH) <sub>14</sub> O <sub>6</sub> (cr)	- 7611.662 <sup>(b)</sup> ±20.290			
SnBr <sup>+</sup>	- 138.832 <sup>(b)</sup> ±1.083			
SnBr <sub>2</sub> (aq)	- 246.336 <sup>(b)</sup> ±1.280			
SnBr <sub>2</sub> (cr)	- 237.876 <sup>(a)</sup> ±2.304	- 252.900 ±2.300	153.000 ±0.300	78.970 ±0.160
SnBr <sub>2</sub> (g)	- 155.751 <sup>(a)</sup> ±4.301	- 118.300 <sup>(b)</sup> ±4.300	329.000 ±0.100	56.400 ±0.100
SnBr <sub>3</sub> <sup>-</sup>	- 349.958 <sup>(b)</sup> ±1.649			
SnBr <sub>4</sub> (cr)	- 359.497 <sup>(a)</sup> ±3.006	- 388.000 ±3.000	260.000 ±0.260	136.000 ±0.500
SnBr <sub>4</sub> (g)	- 341.373 <sup>(a)</sup> ±4.504	- 324.200 <sup>(b)</sup> ±4.500	413.200 ±0.100	103.300 ±0.200
SnI <sub>2</sub> (cr)	- 153.143 <sup>(a)</sup> ±2.917	- 153.000 ±2.900	168.800 ±1.000	78.450 ±0.160
SnI <sub>2</sub> (g)	- 60.390 <sup>(a)</sup> ±3.102	- 8.100 <sup>(b)</sup> ±3.100	342.700 ±0.100	56.700 ±0.100
SnI <sub>4</sub> (cr)	- 207.476 <sup>(a)</sup> ±2.623	- 207.700 ±2.600	282.710 ±1.000	131.960 ±0.260
SnI <sub>4</sub> (g)	- 168.166 <sup>(a)</sup> ±4.005	- 118.900 <sup>(b)</sup> ±4.000	448.700 ±0.200	105.500 ±0.200
SnS(cr)	- 107.688 <sup>(a)</sup> ±4.008	- 109.600 ±4.000	76.820 ±0.840	49.200 ±0.500
Sn <sub>2</sub> S <sub>3</sub> (cr)	- 253.588 <sup>(a)</sup> ±21.076	- 264.000 ±21.000	163.600 ±6.000	118.500 ±1.600
SnS <sub>2</sub> (cr)	- 143.185 <sup>(a)</sup> ±4.025	- 151.500 ±4.000	87.400 ±1.500	68.900 ±1.000
Cu <sub>2</sub> Sn <sub>4</sub> S <sub>9</sub> (cr)	- 165.599 <sup>(a)</sup> ±8.278	- 141.600 ±6.300	640.000 ±18.000	
Cu <sub>2</sub> SnS <sub>3</sub> (cr)	- 169.486 <sup>(a)</sup> ±5.509	- 150.000 ±5.500	279.000 ±1.000	

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Table III-1 (Continued)

Compound	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Cu <sub>4</sub> SnS <sub>4</sub> (cr)	- 251.212 <sup>(a)</sup> ±11.132	- 220.800 ±9.400	414.000 ±20.000	230.000 ±0.200
Cu <sub>8</sub> SnS <sub>6</sub> (cr)				365.000 ±29.000
SnSO <sub>4</sub> (aq)	- 790.973 <sup>(b)</sup> ±1.517			
Sn <sub>3</sub> (OH) <sub>2</sub> OSO <sub>4</sub> (cr)	- 1566.191 ±2.337			
SnSCN <sup>+</sup>	56.748 <sup>(b)</sup> ±5.662			
SnNO <sub>3</sub> <sup>+</sup>	- 145.433 <sup>(b)</sup> ±1.843			
Sn(NO <sub>3</sub> ) <sub>2</sub> (aq)	- 256.912 <sup>(b)</sup> ±3.153			
Ag <sub>6</sub> Sn <sub>4</sub> P <sub>12</sub> Ge <sub>6</sub> (cr)	- 76.485 <sup>(a)</sup> ±8.064	- 147.000 ±7.000	903.130 ±13.000	628.820 ±9.400
Sn <sub>4</sub> As <sub>3</sub> (cr)			327.000 ±1.600	180.500 ±0.900
SnAs(cr)	- 10.013 <sup>(a)</sup> ±3.209	- 9.500 ±3.200	88.000 ±0.500	51.200 ±0.260

(a) Value calculated internally using  $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \sum S_{m,i}^\circ$ .

(b) Value calculated internally from reaction data (see Table III-2).

Table III-2: Selected thermodynamic data for reactions involving tin compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapters V to XI. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ·mol <sup>-1</sup> )	(kJ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Sn <sup>4+</sup>	2H <sup>+</sup> + Sn <sup>2+</sup> $\rightleftharpoons$ H <sub>2</sub> (g) + Sn <sup>4+</sup>	- 12.982	74.101		
		±0.676	±3.859		
SnOH <sup>+</sup>	H <sub>2</sub> O(l) + Sn <sup>2+</sup> $\rightleftharpoons$ H <sup>+</sup> + SnOH <sup>+</sup>	- 3.530	20.149		
		±0.400	±2.283		
Sn <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	4H <sub>2</sub> O(l) + 3Sn <sup>2+</sup> $\rightleftharpoons$ 4H <sup>+</sup> + Sn <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	- 5.600	31.965		
		±0.470	±2.683		
Sn(OH) <sub>2</sub> (aq)	2H <sub>2</sub> O(l) + Sn <sup>2+</sup> $\rightleftharpoons$ 2H <sup>+</sup> + Sn(OH) <sub>2</sub> (aq)	- 7.680	43.838		
		±0.400	±2.283		
Sn(OH) <sub>4</sub> (aq)	2H <sub>2</sub> O(l) + SnO <sub>2</sub> (cass) $\rightleftharpoons$ Sn(OH) <sub>4</sub> (aq)	- 8.060	46.007		
		±0.110	±0.628		
Sn(OH) <sub>3</sub> <sup>-</sup>	3H <sub>2</sub> O(l) + Sn <sup>2+</sup> $\rightleftharpoons$ 3H <sup>+</sup> + Sn(OH) <sub>3</sub> <sup>-</sup>	- 17.000	97.037		
		±0.600	±3.425		
Sn(OH) <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O(l) + OH <sup>-</sup> + SnO(cr) $\rightleftharpoons$ Sn(OH) <sub>3</sub> <sup>-</sup>	- 0.840	4.795		
		±0.020	±0.114		
Sn(OH) <sub>5</sub> <sup>-</sup>	H <sub>2</sub> O(l) + Sn(OH) <sub>4</sub> (aq) $\rightleftharpoons$ H <sup>+</sup> + Sn(OH) <sub>5</sub> <sup>-</sup>	- 8.600	49.089		
		±0.400	±2.283		

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Table III-2 (Continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ·mol <sup>-1</sup> )	(kJ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Sn(OH) <sub>6</sub> <sup>2-</sup>	2H <sub>2</sub> O(l) + Sn(OH) <sub>4</sub> (aq) ⇌ 2H <sup>+</sup> + Sn(OH) <sub>6</sub> <sup>2-</sup>	-18.670	106.569		
		±0.300	±1.712		
SnCl <sub>4</sub> (g)	SnCl <sub>4</sub> (l) ⇌ SnCl <sub>4</sub> (g)			38.500	
				±0.150	
SnF <sup>+</sup>	F <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnF <sup>+</sup>	5.250	-29.967		
		±0.190	±1.085		
SnF <sub>2</sub> (aq)	2F <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnF <sub>2</sub> (aq)	8.890	-50.744		
		±0.210	±1.199		
SnF <sub>2</sub> (g)	SnF <sub>2</sub> (cr) ⇌ SnF <sub>2</sub> (g)			166.000	
				±2.000	
SnF <sub>3</sub> <sup>-</sup>	3F <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnF <sub>3</sub> <sup>-</sup>	11.500	-65.642		
		±1.000	±5.708		
SnCl <sup>+</sup>	Cl <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnCl <sup>+</sup>	1.520	-8.676	12.700	71.696
		±0.200	±1.142	±2.300	±8.612
SnCl <sub>2</sub> (aq)	2Cl <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnCl <sub>2</sub> (aq)	2.170	-12.386	19.700	107.618
		±0.170	±0.970	±4.500	±15.440
SnCl <sub>2</sub> (g)	SnCl <sub>2</sub> (cr) ⇌ SnCl <sub>2</sub> (g)			130.400	
				±3.700	
SnCl <sub>3</sub> <sup>-</sup>	3Cl <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnCl <sub>3</sub> <sup>-</sup>	2.132	-12.170		
		±0.190	±1.085		
SnCl <sub>4</sub> <sup>2-</sup>	4Cl <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnCl <sub>4</sub> <sup>2-</sup>	2.030	-11.587		
		±0.400	±2.283		

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Table III-2 (Continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ·mol <sup>-1</sup> )	(kJ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Sn <sub>21</sub> Cl <sub>16</sub> (OH) <sub>14</sub> O <sub>6</sub> (cr)	16Cl <sup>-</sup> + 20H <sub>2</sub> O(l) + 21Sn <sup>2+</sup> ⇌ 26H <sup>+</sup> + Sn <sub>21</sub> Cl <sub>16</sub> (OH) <sub>14</sub> O <sub>6</sub> (cr)	34.020	- 194.188		
		±3.360	±19.179		
SnBr <sup>+</sup>	Br <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnBr <sup>+</sup>	1.330	- 7.592		
		±0.180	±1.027		
SnBr <sub>2</sub> (aq)	2Br <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnBr <sub>2</sub> (aq)	1.970	- 11.245		
		±0.210	±1.199		
SnBr <sub>2</sub> (g)	SnBr <sub>2</sub> (cr) ⇌ SnBr <sub>2</sub> (g)			134.600	
				±2.000	
SnBr <sub>4</sub> (g)	SnBr <sub>4</sub> (cr) ⇌ SnBr <sub>4</sub> (g)			63.800	
				±1.500	
SnBr <sub>3</sub> <sup>-</sup>	3Br <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnBr <sub>3</sub> <sup>-</sup>	1.930	- 11.017		
		±0.270	±1.541		
SnI <sub>2</sub> (g)	SnI <sub>2</sub> (cr) ⇌ SnI <sub>2</sub> (g)			144.900	
				±2.500	
SnI <sub>4</sub> (g)	SnI <sub>4</sub> (cr) ⇌ SnI <sub>4</sub> (g)			88.600	
				±2.600	
SnSCN <sup>+</sup>	SCN <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnSCN <sup>+</sup>	1.500	- 8.562		
		±0.700	±3.996		
SnSO <sub>4</sub> (aq)	SO <sub>4</sub> <sup>2-</sup> + Sn <sup>2+</sup> ⇌ SnSO <sub>4</sub> (aq)	3.430	- 19.579		
		±0.250	±1.427		
SnNO <sub>3</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup> + Sn <sup>2+</sup> ⇌ SnNO <sub>3</sub> <sup>+</sup>	1.270	- 7.249		
		±0.310	±1.769		

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Table III-2 (Continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ·mol <sup>-1</sup> )	(kJ·mol <sup>-1</sup> )	(J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Sn(NO <sub>3</sub> ) <sub>2</sub> (aq)	2NO <sub>3</sub> <sup>-</sup> + Sn <sup>2+</sup> ⇌ Sn(NO <sub>3</sub> ) <sub>2</sub> (aq)	1.390	-7.934		
		±0.530	±3.025		

(a) Value calculated internally using  $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \Delta_r S_m^\circ$ .

(b) Value of  $\log_{10} K^\circ$  calculated internally from  $\Delta_r G_m^\circ$ .

Table III-3: Selected temperature coefficients for heat capacities in the form  $C_{p,m}^o(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + fT^3$  (Eq. (II.54)). The functions are valid between the temperatures  $T_{\min}$  and  $T_{\max}$  (in K). Units for  $C_{p,m}^o$  are  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Compound	$a$	$b$	$c$	$d$	$e$	$f$	$g$	$T_{\min}$	$T_{\max}$
$\beta$ -Sn	34.297	$-2.9957 \times 10^{-2}$	$5.0794 \times 10^{-5}$		$-2.461 \times 10^5$			298	505
SnO(cr) <sup>(a)</sup>	77.816	$-25.295$						4.3	312
SnO <sub>2</sub> (cr) <sup>(b)</sup>	$1.7419 \times 10^{-1}$	$-2.1858 \times 10^{-4}$	$4.4830 \times 10^3$	$-2.9144 \times 10^4$	$1.1389 \times 10^5$	$-1.0659 \times 10^3$		16	336
SnO <sub>2</sub> (cr) <sup>(b)</sup>	$2.2817 \times 10^{-1}$	$-3.8118 \times 10^{-5}$	$-4.2485 \times 10^5$	$2.5506 \times 10^7$	$-4.9696 \times 10^8$	$3.2586 \times 10^4$		298.15	1500
SnH <sub>4</sub> (g)	51.80	0.03766			$-1.130 \times 10^6$			298	600
$\alpha$ -PbSnF <sub>4</sub>	$-235.111$	2.42159	$-0.00365$					270	353
$\beta$ -PbSnF <sub>4</sub>	$-333.279$	4.15949	$-0.01166$			$1.09843 \times 10^{-5}$		353	600
BaSnF <sub>4</sub> (cr)	$-9.43794$	1.03157	$-0.00219$			$1.62305 \times 10^{-6}$		290	600
SrSnF <sub>4</sub> (cr)	$-172.407$	2.29374	$-0.00549$			$4.67657 \times 10^{-6}$		290	600
SnCl <sub>2</sub> (cr) <sup>(c)</sup>	$-4.14601$	0.68493	0.0067938	$-1.36775 \times 10^{-4}$	$8.35148 \times 10^{-7}$	$-2.24917 \times 10^{-9}$	$2.2757 \times 10^{-12}$	9	304
SnBr <sub>2</sub> (cr)	41.097	$1.2158 \times 10^{-1}$	$-6.3618 \times 10^{-5}$		$6.4755 \times 10^5$			298	507
SnBr <sub>2</sub> (l)	88.328	$-4.6988 \times 10^{-3}$	$4.0879 \times 10^{-5}$		$-5.4090 \times 10^4$			507	1000
SnBr <sub>2</sub> (g)	58.169	$1.5400 \times 10^{-5}$	$-1.7100 \times 10^{-9}$		$-1.5911 \times 10^5$			298	6000
SnI <sub>2</sub> (cr)	76.62	0.0228		$-1459$	8107			11.7	312.7
SnBr <sub>4</sub> (cr) <sup>(d)</sup>	174.35	0.012684	$5.0467 \times 10^{-6}$	1002.9	492.24		$-856.07$	6.66	336.2
SnI <sub>4</sub> (cr)	121.2	$6.190 \times 10^{-2}$		$-2113$	10731			11.5	308
SnF <sub>2</sub> (g)	29.68	0.09146	$-8.1756 \times 10^{-5}$					100	600
$\alpha$ -SnS <sup>(e)</sup>	$-19.1440$	11.6659	$-1.99273$	0.114905				100	875
Sn <sub>2</sub> S <sub>3</sub> (cr) <sup>(e)</sup>	$-19.8237$	11.6663	$-1.85497$	0.0991872				100	610
Sn <sub>2</sub> (cr) <sup>(e)</sup>	$-23.6488$	13.2230	$-2.10132$	0.112224				100	1005
Ag <sub>6</sub> Sn <sub>4</sub> P <sub>12</sub> Ge <sub>6</sub> (cr)	556.2	0.3406			$-2.572 \times 10^6$			230	325
SnAs(cr) <sup>(f)</sup>	61.44	$-49.17$						5	40

(Continued on next page)



Table III-3 (Continued)

Compound	a	b	c	d	e	f	g	$T_{\min}$	$T_{\max}$
SnAs(cr) <sup>(e)</sup>	-6.399	0.04747	-9602		94539		1288	40	313
Sn <sub>4</sub> As <sub>3</sub> (cr) <sup>(f)</sup>	167.9	-35.55						5	40
Sn <sub>4</sub> As <sub>3</sub> (cr) <sup>(g)</sup>	-30.22	0.1828		-33393	333880		4554	40	315

(a) Equation of the form  $C_{p,m}^o(T) = a(T/K)^{b(K/T)}$ , see Sections VII.2.2.2 and VII.2.2.3.

(b) Equations of the form  $C_{p,m}^o(T) - C_{p,m}^o(T_0) = a[T/K - T_0/K] + b[(T/K)^2 - (T_0/K)^2] + c[(T/K)^{-1} - (T_0/K)^{-1}] + d[(T/K)^{-2} - (T_0/K)^{-2}] + e[(T/K)^{-3} - (T_0/K)^{-3}] + f[(T/K)^{-0.5} - (T_0/K)^{-0.5}]$ , with  $C_{p,m}^o(\text{SnO}_2, \text{cr}, T_0 = 16 \text{ K}) = 0.168 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $C_{p,m}^o(\text{SnO}_2, \text{cr}, T_0 = 298.15 \text{ K}) = 55.26 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively.

The same equation was applied to the high temperature interval because  $C_{p,m}^o(\text{SnO}_2, \text{cr}, 298.15 \text{ K})$  was selected from low-temperature data and had therefore to be treated as an invariant in the regression analysis, see Section VII.2.3.2.

(c) Equation of the form  $C_{p,m}^o(T) = a + b(T/K) + c(T/K)^2 + d(T/K)^3 + e(T/K)^4 + f(T/K)^5 + g(T/K)^6$ , see Section VIII.1.2.1.

(d) Equation of the form  $C_{p,m}^o(T) = a + b(T/K) + c(T/K)^2 + d(T/K)^{-1} + e(T/K)^{-2} + g(T/K)^{-0.5}$ , see Section VIII.1.3.2.

(e) Equation of the form  $C_{p,m}^o(T) = \exp\{a + b[\ln(T/K)] + c[\ln(T/K)]^2 + d[\ln(T/K)]^3\}$ , see Section IX.1.1.2.

(f) Equation of the form  $C_{p,m}^o(T) = a \times \exp[b(K/T)]$ , see Sections X.3.1.1 and X.3.1.2.

(g) Equation of the form  $C_{p,m}^o(T) = a + b(T/K) + d(T/K)^{-1} + e(T/K)^{-2} + g(T/K)^{-0.5}$ , see Sections X.3.1.1 and X.3.1.2.



# Chapter IV

## Selected auxiliary data

This chapter presents the chemical thermodynamic data for auxiliary compounds and complexes which are used within the NEA TDB Project. Most of these auxiliary species are used in the evaluation of the recommended tin data in Tables III-1, III-2 and III-3. It is therefore essential to always use these auxiliary data in conjunction with the selected data for tin. The use of other auxiliary data can lead to inconsistencies and erroneous results.

The values in the tables of this chapter for auxiliary compounds and complexes are either CODATA Key Values, taken from [1989COX/WAG], or were evaluated within the NEA TDB Project, as described in the corresponding chapters of the uranium review [1992GRE/FUG], the technetium review [1999RAR/RAN], the neptunium and plutonium review [2001LEM/FUG], the Update review [2003GUI/FAN], the nickel review [2005GAM/BUG] and the selenium review [2005OLI/NOL].

Table IV-1 contains the selected thermodynamic data of the auxiliary species and Table IV-2 the selected thermodynamic data of chemical reactions involving auxiliary species. The reason for listing both reaction data and entropies, enthalpies and Gibbs energies of formation is, as described in Chapter III, that uncertainties in reaction data are often smaller than the derived  $S_m^\circ$ ,  $\Delta_f H_m^\circ$  and  $\Delta_f G_m^\circ$ , due to uncertainty accumulation during the calculations.

All data in Table IV-1 and Table IV-2 refer to a temperature of 298.15 K, the standard state pressure of 0.1 MPa and, for aqueous species and reactions, to the infinite dilution standard state ( $I = 0$ ).

The uncertainties listed below each reaction value in Table IV-2 are total uncertainties, and correspond mainly to the statistically defined 95% confidence interval. The uncertainties listed below each value in Table IV-1 have the following significance:

- for CODATA values from [1989COX/WAG], the  $\pm$  terms have the meaning: “it is probable, but not at all certain, that the true values of the thermodynamic quantities differ from the recommended values given in this report by no more than twice the  $\pm$  terms attached to the recommended values”.
- for values from [1992GRE/FUG], [1999RAR/RAN], [2003GUI/FAN], [2005GAM/BUG] and [2005OLI/NOL], the  $\pm$  terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table IV-2), and from the  $\pm$  terms listed for the necessary CODATA key values.

CODATA [1989COX/WAG] values are available for  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . From the values given for  $\Delta_f H_m^\circ$  and  $S_m^\circ$  the values of  $\Delta_f G_m^\circ$  and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , which were absent from the corresponding Table IV-2 in [1992GRE/FUG], are included in this volume to provide the user of selected data for the organic ligands (*cf.* Chapter III) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Table IV-1 and Table IV-2 may contain more digits than those listed in either [1989COX/WAG] or in the chapters devoted to data selection in [1992GRE/FUG], [1995SIL/BID], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG] and [2005OLI/NOL], because the data in the present chapter are retrieved directly from the computerised data base and rounded to three digits after the decimal point throughout.

Table IV-1: Selected thermodynamic data for auxiliary compounds and complexes adopted in the NEA TDB Project, including the CODATA Key Values [1989COX/WAG]. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in bold typeface are CODATA Key Values and are taken directly from [1989COX/WAG] without further evaluation. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in the chapters devoted to data selection in [1992GRE/FUG], [1995SIL/BID], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG] and [2005OLI/NOL]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
O(g) [1992GRE/FUG]	<b>231.743</b> <sup>(a)</sup> <b>±0.100</b>	<b>249.180</b> <b>±0.100</b>	<b>161.059</b> <b>±0.003</b>	<b>21.912</b> <b>±0.001</b>
O <sub>2</sub> (g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>205.152</b> <b>±0.005</b>	<b>29.378</b> <b>±0.003</b>
H(g) [1992GRE/FUG]	<b>203.276</b> <sup>(a)</sup> <b>±0.006</b>	<b>217.998</b> <b>±0.006</b>	<b>114.717</b> <b>±0.002</b>	<b>20.786</b> <b>±0.001</b>
H <sup>+</sup> [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
H <sub>2</sub> (g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>130.680</b> <b>±0.003</b>	<b>28.836</b> <b>±0.002</b>
D <sub>2</sub> (g) [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	144.958 ±0.005	29.195 ±0.005
T <sub>2</sub> (g) [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	153.327 ±0.005	29.199 ±0.005
OH <sup>-</sup> [1992GRE/FUG]	- <b>157.220</b> <sup>(a)</sup> <b>±0.072</b>	- <b>230.015</b> <b>±0.040</b>	- <b>10.900</b> <b>±0.200</b>	
H <sub>2</sub> O(g) [1992GRE/FUG]	- <b>228.582</b> <sup>(a)</sup> <b>±0.040</b>	- <b>241.826</b> <b>±0.040</b>	<b>188.835</b> <b>±0.010</b>	<b>33.609</b> <b>±0.030</b>
H <sub>2</sub> O(l) [1992GRE/FUG]	- <b>237.140</b> <sup>(a)</sup> <b>±0.041</b>	- <b>285.830</b> <b>±0.040</b>	<b>69.950</b> <b>±0.030</b>	<b>75.351</b> <b>±0.080</b>

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
H <sub>2</sub> O <sub>2</sub> (aq) [1992GRE/FUG]		- 191.170 ±0.100		
He(g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>126.153</b> ±0.002	<b>20.786</b> ±0.001
Ne(g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>146.328</b> ±0.003	<b>20.786</b> ±0.001
Ar(g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>154.846</b> ±0.003	<b>20.786</b> ±0.001
Kr(g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>164.085</b> ±0.003	<b>20.786</b> ±0.001
Xe(g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>169.685</b> ±0.003	<b>20.786</b> ±0.001
F(g) [1992GRE/FUG]	<b>62.280</b> <sup>(a)</sup> ±0.300	<b>79.380</b> ±0.300	<b>158.751</b> ±0.004	<b>22.746</b> ±0.002
F <sup>-</sup> [1992GRE/FUG]	- <b>281.523</b> <sup>(a)</sup> ±0.692	- <b>335.350</b> ±0.650	- <b>13.800</b> ±0.800	
F <sub>2</sub> (g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>202.791</b> ±0.005	<b>31.304</b> ±0.002
HF(aq) [1992GRE/FUG]	- 299.675 ±0.702	- 323.150 ±0.716	88.000 <sup>(a)</sup> ±3.362	
HF(g) [1992GRE/FUG]	- <b>275.400</b> <sup>(a)</sup> ±0.700	- <b>273.300</b> ±0.700	<b>173.779</b> ±0.003	<b>29.137</b> ±0.002
HF <sub>2</sub> <sup>-</sup> [1992GRE/FUG]	- 583.709 ±1.200	- 655.500 ±2.221	92.683 <sup>(a)</sup> ±8.469	
Cl(g) [1992GRE/FUG]	<b>105.305</b> <sup>(a)</sup> ±0.008	<b>121.301</b> ±0.008	<b>165.190</b> ±0.004	<b>21.838</b> ±0.001
Cl <sup>-</sup> [1992GRE/FUG]	- <b>131.217</b> <sup>(a)</sup> ±0.117	- <b>167.080</b> ±0.100	<b>56.600</b> ±0.200	
Cl <sub>2</sub> (g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>223.081</b> ±0.010	<b>33.949</b> ±0.002
ClO <sup>-</sup> [2005OLI/NOL]	- 37.669 <sup>(b)</sup> ±0.962	- 108.300 <sup>(b)</sup> ±1.500	42.560 <sup>(b)</sup> ±9.238	
ClO <sub>2</sub> <sup>-</sup> [1992GRE/FUG]	10.250 ±4.044			
ClO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 7.903 <sup>(a)</sup> ±1.342	- 104.000 ±1.000	162.300 ±3.000	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
ClO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	- 7.890 <sup>(a)</sup> ±0.600	- 128.100 ±0.400	184.000 ±1.500	
HCl(g) [1992GRE/FUG]	- 95.298 <sup>(a)</sup> ±0.100	- 92.310 ±0.100	186.902 ±0.005	29.136 ±0.002
HClO(aq) [2005OLI/NOL]	- 80.023 <sup>(a)</sup> ±0.613	- 125.700 ±1.500	- 126.255 ±5.434	
HClO <sub>2</sub> (aq) [1992GRE/FUG]	- 0.938 ±4.043			
Br(g) [1992GRE/FUG]	82.379 <sup>(a)</sup> ±0.128	111.870 ±0.120	175.018 ±0.004	20.786 ±0.001
Br <sup>-</sup> [1992GRE/FUG]	- 103.850 <sup>(a)</sup> ±0.167	- 121.410 ±0.150	82.550 ±0.200	
Br <sub>2</sub> (aq) [1992GRE/FUG]	4.900 ±1.000			
Br <sub>2</sub> (g) [1992GRE/FUG]	3.105 <sup>(a)</sup> ±0.142	30.910 ±0.110	245.468 ±0.005	36.057 ±0.002
Br <sub>2</sub> (l) [1992GRE/FUG]	0.000	0.000	152.210 ±0.300	
BrO <sup>-</sup> [1992GRE/FUG]	- 32.095 ±1.537			
BrO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	19.070 <sup>(a)</sup> ±0.634	- 66.700 ±0.500	161.500 ±1.300	
HBr(g) [1992GRE/FUG]	- 53.361 <sup>(a)</sup> ±0.166	- 36.290 ±0.160	198.700 ±0.004	29.141 ±0.003
HBrO(aq) [1992GRE/FUG]	- 81.356 <sup>(b)</sup> ±1.527			
I(g) [1992GRE/FUG]	70.172 <sup>(a)</sup> ±0.060	106.760 ±0.040	180.787 ±0.004	20.786 ±0.001
I <sup>-</sup> [1992GRE/FUG]	- 51.724 <sup>(a)</sup> ±0.112	- 56.780 ±0.050	106.450 ±0.300	
I <sub>2</sub> (cr) [1992GRE/FUG]	0.000	0.000	116.140 ±0.300	
I <sub>2</sub> (g) [1992GRE/FUG]	19.323 <sup>(a)</sup> ±0.120	62.420 ±0.080	260.687 ±0.005	36.888 ±0.002
IO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 126.338 <sup>(a)</sup> ±0.779	- 219.700 ±0.500	118.000 ±2.000	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
HI(g) [1992GRE/FUG]	<b>1.700</b> <sup>(a)</sup> <b>±0.110</b>	<b>26.500</b> <b>±0.100</b>	<b>206.590</b> <b>±0.004</b>	<b>29.157</b> <b>±0.003</b>
HIO <sub>3</sub> (aq) [1992GRE/FUG]	- 130.836 ±0.797			
S(cr)(orthorhombic) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>32.054</b> <b>±0.050</b>	<b>22.750</b> <b>±0.050</b>
S(g) [1992GRE/FUG]	<b>236.689</b> <sup>(a)</sup> <b>±0.151</b>	<b>277.170</b> <b>±0.150</b>	<b>167.829</b> <b>±0.006</b>	<b>23.674</b> <b>±0.001</b>
S <sup>2-</sup> [1992GRE/FUG]	120.695 ±11.610			
S <sub>2</sub> (g) [1992GRE/FUG]	<b>79.686</b> <sup>(a)</sup> <b>±0.301</b>	<b>128.600</b> <b>±0.300</b>	<b>228.167</b> <b>±0.010</b>	<b>32.505</b> <b>±0.010</b>
SO <sub>2</sub> (g) [1992GRE/FUG]	- <b>300.095</b> <sup>(a)</sup> <b>±0.201</b>	- <b>296.810</b> <b>±0.200</b>	<b>248.223</b> <b>±0.050</b>	<b>39.842</b> <b>±0.020</b>
SO <sub>3</sub> <sup>2-</sup> [1992GRE/FUG]	- 487.472 ±4.020			
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> [1992GRE/FUG]	- 519.291 ±11.345			
SO <sub>4</sub> <sup>2-</sup> [1992GRE/FUG]	- <b>744.004</b> <sup>(a)</sup> <b>±0.418</b>	- <b>909.340</b> <b>±0.400</b>	<b>18.500</b> <b>±0.400</b>	
HS <sup>-</sup> [1992GRE/FUG]	<b>12.243</b> <sup>(a)</sup> <b>±2.115</b>	- <b>16.300</b> <b>±1.500</b>	<b>67.000</b> <b>±5.000</b>	
H <sub>2</sub> S(aq) [1992GRE/FUG]	- <b>27.648</b> <sup>(a)</sup> <b>±2.115</b>	- <b>38.600</b> <b>±1.500</b>	<b>126.000</b> <b>±5.000</b>	
H <sub>2</sub> S(g) [1992GRE/FUG]	- <b>33.443</b> <sup>(a)</sup> <b>±0.500</b>	- <b>20.600</b> <b>±0.500</b>	<b>205.810</b> <b>±0.050</b>	<b>34.248</b> <b>±0.010</b>
HSO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 528.684 ±4.046			
HS <sub>2</sub> O <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 528.366 ±11.377			
H <sub>2</sub> SO <sub>3</sub> (aq) [1992GRE/FUG]	- 539.187 ±4.072			
HSO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	- <b>755.315</b> <sup>(a)</sup> <b>±1.342</b>	- <b>886.900</b> <b>±1.000</b>	<b>131.700</b> <b>±3.000</b>	
Se(cr) (trigonal) [2005OLI/NOL]	0.000	0.000	42.090 ±0.330	25.090 <sup>(c)</sup> ±0.300

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Se(monoclinic) [2005OLI/NOL]	1.281 <sup>(a)</sup> ±0.184	2.140 ±0.100	44.970 ±0.400	25.090 <sup>(c)</sup> ±0.800
Se(l) [2005OLI/NOL]				<sup>(c)</sup>
Se(g) [2005OLI/NOL]	195.927 <sup>(a)</sup> ±1.524	236.070 <sup>(b)</sup> ±1.521	176.729 ±0.006	20.819 <sup>(c)</sup> ±0.001
Se <sup>2-</sup> [2005OLI/NOL]	128.600 <sup>(b)</sup> ±3.000			
Se <sub>2</sub> (g) [2005OLI/NOL]	92.442 <sup>(a)</sup> ±3.009	141.100 ±3.000	247.380 ±0.400	41.710 <sup>(c)</sup> ±0.200
Se <sub>2</sub> <sup>2-</sup> [2005OLI/NOL]	112.670 <sup>(b)</sup> ±6.294			
Se <sub>3</sub> (g) [2005OLI/NOL]	123.549 <sup>(a)</sup> ±10.439	178.000 ±10.000	308.900 ±10.000	
Se <sub>3</sub> <sup>2-</sup> [2005OLI/NOL]	100.590 <sup>(b)</sup> ±9.198			
Se <sub>4</sub> (g) [2005OLI/NOL]	111.647 <sup>(a)</sup> ±13.406	163.000 ±12.000	340.000 ±20.000	
Se <sub>4</sub> <sup>2-</sup> [2005OLI/NOL]	97.580 <sup>(b)</sup> ±12.149			
Se <sub>5</sub> (g) [2005OLI/NOL]	88.393 <sup>(a)</sup> ±5.256	144.400 ±4.300	398.300 ±10.000	
Se <sub>6</sub> (g) [2005OLI/NOL]	83.638 <sup>(a)</sup> ±4.866	136.100 ±3.800	428.500 ±10.000	
Se <sub>7</sub> (g) [2005OLI/NOL]	92.845 <sup>(a)</sup> ±4.891	150.200 ±4.500	487.000 ±6.000	
Se <sub>8</sub> (g) [2005OLI/NOL]	100.307 <sup>(a)</sup> ±3.580	156.800 ±3.000	526.200 ±6.000	
SeO(g) [2005OLI/NOL]	30.855 <sup>(a)</sup> ±6.218	57.400 ±6.210	233.700 ±1.000	32.520 <sup>(c)</sup> ±0.250
SeO <sub>2</sub> (cr) [2005OLI/NOL]	-171.797 <sup>(a)</sup> ±0.620	-225.390 ±0.600	67.490 ±0.400	58.230 <sup>(c)</sup> ±0.180
SeO <sub>2</sub> (g) [2005OLI/NOL]	-115.166 <sup>(a)</sup> ±2.600	-110.590 <sup>(b)</sup> ±2.571	262.590 ±1.250	43.360 <sup>(c)</sup> ±0.150
SeO <sub>3</sub> (cr) [2005OLI/NOL]	-86.154 <sup>(a)</sup> ±2.222	-163.100 ±2.200	91.740 ±1.000	77.240 <sup>(c)</sup> ±0.790

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
SeO <sub>3</sub> <sup>2-</sup> [2005OLI/NOL]	-362.392 <sup>(b)</sup> ±1.756	-507.160 ±1.130	-5.055 <sup>(a)</sup> ±7.011	
SeO <sub>4</sub> <sup>2-</sup> [2005OLI/NOL]	-439.485 <sup>(b)</sup> ±1.431	-603.500 <sup>(b)</sup> ±3.500	32.965 <sup>(b)</sup> ±12.687	
Se <sub>2</sub> O <sub>5</sub> (cr) [2005OLI/NOL]		-414.590 <sup>(b)</sup> ±2.577		
HSe <sup>-</sup> [2005OLI/NOL]	43.471 <sup>(b)</sup> ±2.024			
H <sub>2</sub> Se(g) [2005OLI/NOL]	15.217 <sup>(a)</sup> ±2.003	29.000 ±2.000	219.000 ±0.100	34.700 <sup>(c)</sup> ±0.100
H <sub>2</sub> Se(aq) [2005OLI/NOL]	21.495 <sup>(b)</sup> ±2.003	14.300 <sup>(b)</sup> ±2.022	148.637 <sup>(b)</sup> ±1.029	
HSeO <sub>3</sub> <sup>-</sup> [2005OLI/NOL]	-410.112 <sup>(b)</sup> ±1.166	-512.330 ±1.010	137.656 <sup>(a)</sup> ±5.184	
HSeO <sub>4</sub> <sup>-</sup> [2005OLI/NOL]	-449.474 <sup>(b)</sup> ±1.312	-582.700 <sup>(d)</sup> ±4.700	136.232 <sup>(a)</sup> ±16.370	
H <sub>2</sub> SeO <sub>3</sub> (cr) [2005OLI/NOL]		-524.720 <sup>(b)</sup> ±0.650		
H <sub>2</sub> SeO <sub>3</sub> (aq) [2005OLI/NOL]	-425.181 <sup>(b)</sup> ±0.849	-505.320 ±0.650	211.710 <sup>(a)</sup> ±3.601	
H <sub>2</sub> SeO <sub>4</sub> (cr) [2005OLI/NOL]		-530.500 ±1.880		
Te(cr) [1992GRE/FUG]	0.000	0.000	49.221 ±0.050	25.550 ±0.100
TeO <sub>2</sub> (cr) [2003GUI/FAN]	-265.996 <sup>(a)</sup> ±2.500	-321.000 ±2.500	69.890 ±0.150	60.670 ±0.150
N(g) [1992GRE/FUG]	<b>455.537<sup>(a)</sup></b> <b>±0.400</b>	<b>472.680</b> <b>±0.400</b>	<b>153.301</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
N <sub>2</sub> (g) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>191.609</b> <b>±0.004</b>	<b>29.124</b> <b>±0.001</b>
N <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	348.200 ±2.000	275.140 ±1.000	107.710 <sup>(a)</sup> ±7.500	
NO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	-110.794 <sup>(a)</sup> <b>±0.417</b>	-206.850 <b>±0.400</b>	<b>146.700</b> <b>±0.400</b>	
HN <sub>3</sub> (aq) [1992GRE/FUG]	321.372 ±2.051	260.140 ±10.050	147.381 ±34.403	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
NH <sub>3</sub> (aq) [1992GRE/FUG]	- 26.673 ±0.305	- 81.170 ±0.326	109.040 ±0.913	
NH <sub>3</sub> (g) [1992GRE/FUG]	<b>- 16.407</b> <sup>(a)</sup> <b>±0.350</b>	<b>- 45.940</b> <b>±0.350</b>	<b>192.770</b> <b>±0.050</b>	<b>35.630</b> <b>±0.005</b>
NH <sub>4</sub> <sup>+</sup> [1992GRE/FUG]	<b>- 79.398</b> <sup>(a)</sup> <b>±0.278</b>	<b>- 133.260</b> <b>±0.250</b>	<b>111.170</b> <b>±0.400</b>	
P(am)(red) [1992GRE/FUG]		- 7.500 ±2.000		
P(cr)(white, cubic) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>41.090</b> <b>±0.250</b>	<b>23.824</b> <b>±0.200</b>
P(g) [1992GRE/FUG]	<b>280.093</b> <sup>(a)</sup> <b>±1.003</b>	<b>316.500</b> <b>±1.000</b>	<b>163.199</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
P <sub>2</sub> (g) [1992GRE/FUG]	<b>103.469</b> <sup>(a)</sup> <b>±2.006</b>	<b>144.000</b> <b>±2.000</b>	<b>218.123</b> <b>±0.004</b>	<b>32.032</b> <b>±0.002</b>
P <sub>4</sub> (g) [1992GRE/FUG]	<b>24.419</b> <sup>(a)</sup> <b>±0.448</b>	<b>58.900</b> <b>±0.300</b>	<b>280.010</b> <b>±0.500</b>	<b>67.081</b> <b>±1.500</b>
PO <sub>4</sub> <sup>3-</sup> [1992GRE/FUG]	- 1025.491 ±1.576	- 1284.400 ±4.085	- 220.970 ±12.846	
P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> [1992GRE/FUG]	- 1935.503 ±4.563			
HPO <sub>4</sub> <sup>2-</sup> [1992GRE/FUG]	<b>- 1095.985</b> <sup>(a)</sup> <b>±1.567</b>	<b>- 1299.000</b> <b>±1.500</b>	<b>- 33.500</b> <b>±1.500</b>	
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	<b>- 1137.152</b> <sup>(a)</sup> <b>±1.567</b>	<b>- 1302.600</b> <b>±1.500</b>	<b>92.500</b> <b>±1.500</b>	
H <sub>3</sub> PO <sub>4</sub> (aq) [1992GRE/FUG]	- 1149.367 ±1.576	- 1294.120 ±1.616	161.912 ±2.575	
HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> [1992GRE/FUG]	- 1989.158 ±4.482			
H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> [1992GRE/FUG]	- 2027.117 ±4.445			
H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> [1992GRE/FUG]	- 2039.960 ±4.362			
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) [1992GRE/FUG]	- 2045.668 ±3.299	- 2280.210 ±3.383	274.919 ±6.954	
As(cr) [1992GRE/FUG]	0.000	0.000	35.100 ±0.600	24.640 ±0.500

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
AsO <sub>2</sub> <sup>-</sup> [1992GRE/FUG]	- 350.022 <sup>(a)</sup> ±4.008	- 429.030 ±4.000	40.600 ±0.600	
AsO <sub>4</sub> <sup>3-</sup> [1992GRE/FUG]	- 648.360 <sup>(a)</sup> ±4.008	- 888.140 ±4.000	- 162.800 ±0.600	
As <sub>2</sub> O <sub>5</sub> (cr) [1992GRE/FUG]	- 782.449 <sup>(a)</sup> ±8.016	- 924.870 ±8.000	105.400 ±1.200	116.520 ±0.800
As <sub>4</sub> O <sub>6</sub> (cubic) [1992GRE/FUG]	- 1152.445 <sup>(a)</sup> ±16.032	- 1313.940 ±16.000	214.200 ±2.400	191.290 ±0.800
As <sub>4</sub> O <sub>6</sub> (monoclinic) [1992GRE/FUG]	- 1154.009 <sup>(a)</sup> ±16.041	- 1309.600 ±16.000	234.000 ±3.000	
As <sub>4</sub> O <sub>6</sub> (g) [2005GAM/BUG]	- 1092.716 <sup>(a)</sup> ±16.116	- 1196.250 ±16.000	408.600 ±6.000	
HAsO <sub>2</sub> (aq) [1992GRE/FUG]	- 402.925 <sup>(a)</sup> ±4.008	- 456.500 ±4.000	125.900 ±0.600	
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 587.078 <sup>(a)</sup> ±4.008	- 714.790 ±4.000	110.500 ±0.600	
H <sub>3</sub> AsO <sub>3</sub> (aq) [1992GRE/FUG]	- 639.681 <sup>(a)</sup> ±4.015	- 742.200 ±4.000	195.000 ±1.000	
HAsO <sub>4</sub> <sup>2-</sup> [1992GRE/FUG]	- 714.592 <sup>(a)</sup> ±4.008	- 906.340 ±4.000	- 1.700 ±0.600	
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	- 753.203 <sup>(a)</sup> ±4.015	- 909.560 ±4.000	117.000 ±1.000	
H <sub>3</sub> AsO <sub>4</sub> (aq) [1992GRE/FUG]	- 766.119 <sup>(a)</sup> ±4.015	- 902.500 ±4.000	184.000 ±1.000	
(As <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> · 5 H <sub>2</sub> O(cr) [1992GRE/FUG]		- 4248.400 ±24.000		
Sb(cr) [1992GRE/FUG]	0.000	0.000	45.520 ±0.210	25.260 ±0.200
Bi(cr) [2001LEM/FUG]	0.000	0.000	56.740 ±0.420	25.410 ±0.200
C(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>5.740</b> <b>±0.100</b>	<b>8.517</b> <b>±0.080</b>
C(g) [1992GRE/FUG]	<b>671.254</b> <sup>(a)</sup> <b>±0.451</b>	<b>716.680</b> <b>±0.450</b>	<b>158.100</b> <b>±0.003</b>	<b>20.839</b> <b>±0.001</b>
CO(g) [1992GRE/FUG]	- <b>137.168</b> <sup>(a)</sup> <b>±0.173</b>	- <b>110.530</b> <b>±0.170</b>	<b>197.660</b> <b>±0.004</b>	<b>29.141</b> <b>±0.002</b>

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
CO <sub>2</sub> (aq) [1992GRE/FUG]	- 385.970 <sup>(a)</sup> ±0.270	- 413.260 ±0.200	119.360 ±0.600	
CO <sub>2</sub> (g) [1992GRE/FUG]	- 394.373 <sup>(a)</sup> ±0.133	- 393.510 ±0.130	213.785 ±0.010	37.135 ±0.002
CO <sub>3</sub> <sup>2-</sup> [1992GRE/FUG]	- 527.900 <sup>(a)</sup> ±0.390	- 675.230 ±0.250	- 50.000 ±1.000	
HCO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 586.845 <sup>(a)</sup> ±0.251	- 689.930 ±0.200	98.400 ±0.500	
CN <sup>-</sup> [2005OLI/NOL]	166.939 <sup>(b)</sup> ±2.519	147.350 <sup>(b)</sup> ±3.541	101.182 <sup>(b)</sup> ±8.475	
HCN(aq) [2005OLI/NOL]	114.368 <sup>(b)</sup> ±2.517	103.750 <sup>(b)</sup> ±3.536	131.271 <sup>(b)</sup> ±8.440	
HCN(g) [2005OLI/NOL]	119.517 <sup>(a)</sup> ±2.500	129.900 ±2.500	201.710 ±0.100	
SCN <sup>-</sup> [1992GRE/FUG]	92.700 ±4.000	76.400 ±4.000	144.268 <sup>(a)</sup> ±18.974	
Si(cr) [1992GRE/FUG]	0.000	0.000	18.810 ±0.080	19.789 ±0.030
Si(g) [1992GRE/FUG]	405.525 <sup>(a)</sup> ±8.000	450.000 ±8.000	167.981 ±0.004	22.251 ±0.001
SiO <sub>2</sub> (α-quartz) [1992GRE/FUG]	- 856.287 <sup>(a)</sup> ±1.002	- 910.700 ±1.000	41.460 ±0.200	44.602 ±0.300
SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> [1992GRE/FUG]	- 1175.651 ±1.265	- 1381.960 ±15.330	- 1.488 ±51.592	
SiO(OH) <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	- 1251.740 ±1.162	- 1431.360 ±3.743	88.024 ±13.144	
Si(OH) <sub>4</sub> (aq) [1992GRE/FUG]	- 1307.735 <sup>(b)</sup> ±1.156	- 1456.960 <sup>(b)</sup> ±3.163	189.973 <sup>(b)</sup> ±11.296	
Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>2-</sup> [1992GRE/FUG]	- 2269.878 ±2.878			
Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>-</sup> [1992GRE/FUG]	- 2332.096 ±2.878			
Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3-</sup> [1992GRE/FUG]	- 3048.536 ±3.870			
Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3-</sup> [1992GRE/FUG]	- 3291.955 ±3.869			

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Si <sub>3</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4-</sup> [1992GRE/FUG]	- 4075.179 ±5.437			
Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3-</sup> [1992GRE/FUG]	- 4136.826 ±4.934			
SiF <sub>4</sub> (g) [1992GRE/FUG]	- 1572.773 <sup>(a)</sup> ±0.814	- 1615.000 ±0.800	282.760 ±0.500	73.622 ±0.500
Ge(cr) [1992GRE/FUG]	0.000	0.000	31.090 ±0.150	23.222 ±0.100
Ge(g) [1992GRE/FUG]	331.209 <sup>(a)</sup> ±3.000	372.000 ±3.000	167.904 ±0.005	30.733 ±0.001
GeO <sub>2</sub> (tetragonal) [1992GRE/FUG]	- 521.404 <sup>(a)</sup> ±1.002	- 580.000 ±1.000	39.710 ±0.150	50.166 ±0.300
GeF <sub>4</sub> (g) [1992GRE/FUG]	- 1150.018 <sup>(a)</sup> ±0.584	- 1190.200 ±0.500	301.900 ±1.000	81.602 ±1.000
Pb(cr) [1992GRE/FUG]	0.000	0.000	64.800 ±0.300	26.650 ±0.100
Pb(g) [1992GRE/FUG]	162.232 <sup>(a)</sup> ±0.805	195.200 ±0.800	175.375 ±0.005	20.786 ±0.001
Pb <sup>2+</sup> [1992GRE/FUG]	- 24.238 <sup>(a)</sup> ±0.399	0.920 ±0.250	18.500 ±1.000	
PbSO <sub>4</sub> (cr) [1992GRE/FUG]	- 813.036 <sup>(a)</sup> ±0.447	- 919.970 ±0.400	148.500 ±0.600	
B(cr) [1992GRE/FUG]	0.000	0.000	5.900 ±0.080	11.087 ±0.100
B(g) [1992GRE/FUG]	521.012 <sup>(a)</sup> ±5.000	565.000 ±5.000	153.436 ±0.015	20.796 ±0.005
B <sub>2</sub> O <sub>3</sub> (cr) [1992GRE/FUG]	- 1194.324 <sup>(a)</sup> ±1.404	- 1273.500 ±1.400	53.970 ±0.300	62.761 ±0.300
B(OH) <sub>3</sub> (aq) [1992GRE/FUG]	- 969.268 <sup>(a)</sup> ±0.820	- 1072.800 ±0.800	162.400 ±0.600	
B(OH) <sub>3</sub> (cr) [1992GRE/FUG]	- 969.667 <sup>(a)</sup> ±0.820	- 1094.800 ±0.800	89.950 ±0.600	86.060 ±0.400
BF <sub>3</sub> (g) [1992GRE/FUG]	- 1119.403 <sup>(a)</sup> ±0.803	- 1136.000 ±0.800	254.420 ±0.200	50.463 ±0.100
Al(cr) [1992GRE/FUG]	0.000	0.000	28.300 ±0.100	24.200 ±0.070

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Al(g) [1992GRE/FUG]	<b>289.376</b> <sup>(a)</sup> <b>±4.000</b>	<b>330.000</b> <b>±4.000</b>	<b>164.554</b> <b>±0.004</b>	<b>21.391</b> <b>±0.001</b>
Al <sup>3+</sup> [1992GRE/FUG]	<b>-491.507</b> <sup>(a)</sup> <b>±3.338</b>	<b>-538.400</b> <b>±1.500</b>	<b>-325.000</b> <b>±10.000</b>	
Al <sub>2</sub> O <sub>3</sub> (corundum) [1992GRE/FUG]	<b>-1582.257</b> <sup>(a)</sup> <b>±1.302</b>	<b>-1675.700</b> <b>±1.300</b>	<b>50.920</b> <b>±0.100</b>	<b>79.033</b> <b>±0.200</b>
AlF <sub>3</sub> (cr) [1992GRE/FUG]	<b>-1431.096</b> <sup>(a)</sup> <b>±1.309</b>	<b>-1510.400</b> <b>±1.300</b>	<b>66.500</b> <b>±0.500</b>	<b>75.122</b> <b>±0.400</b>
Tl <sup>+</sup> [1999RAR/RAN]	<b>-32.400</b> <b>±0.300</b>			
Zn(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>41.630</b> <b>±0.150</b>	<b>25.390</b> <b>±0.040</b>
Zn(g) [1992GRE/FUG]	<b>94.813</b> <sup>(a)</sup> <b>±0.402</b>	<b>130.400</b> <b>±0.400</b>	<b>160.990</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Zn <sup>2+</sup> [1992GRE/FUG]	<b>-147.203</b> <sup>(a)</sup> <b>±0.254</b>	<b>-153.390</b> <b>±0.200</b>	<b>-109.800</b> <b>±0.500</b>	
ZnO(cr) [1992GRE/FUG]	<b>-320.479</b> <sup>(a)</sup> <b>±0.299</b>	<b>-350.460</b> <b>±0.270</b>	<b>43.650</b> <b>±0.400</b>	
Cd(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>51.800</b> <b>±0.150</b>	<b>26.020</b> <b>±0.040</b>
Cd(g) [1992GRE/FUG]	<b>77.230</b> <sup>(a)</sup> <b>±0.205</b>	<b>111.800</b> <b>±0.200</b>	<b>167.749</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Cd <sup>2+</sup> [1992GRE/FUG]	<b>-77.733</b> <sup>(a)</sup> <b>±0.750</b>	<b>-75.920</b> <b>±0.600</b>	<b>-72.800</b> <b>±1.500</b>	
CdO(cr) [1992GRE/FUG]	<b>-228.661</b> <sup>(a)</sup> <b>±0.602</b>	<b>-258.350</b> <b>±0.400</b>	<b>54.800</b> <b>±1.500</b>	
CdSO <sub>4</sub> ·2.667 H <sub>2</sub> O(cr) [1992GRE/FUG]	<b>-1464.959</b> <sup>(a)</sup> <b>±0.810</b>	<b>-1729.300</b> <b>±0.800</b>	<b>229.650</b> <b>±0.400</b>	
Hg(g) [1992GRE/FUG]	<b>31.842</b> <sup>(a)</sup> <b>±0.054</b>	<b>61.380</b> <b>±0.040</b>	<b>174.971</b> <b>±0.005</b>	<b>20.786</b> <b>±0.001</b>
Hg(l) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>75.900</b> <b>±0.120</b>	
Hg <sup>2+</sup> [1992GRE/FUG]	<b>164.667</b> <sup>(a)</sup> <b>±0.313</b>	<b>170.210</b> <b>±0.200</b>	<b>-36.190</b> <b>±0.800</b>	
Hg <sub>2</sub> <sup>2+</sup> [1992GRE/FUG]	<b>153.567</b> <sup>(a)</sup> <b>±0.559</b>	<b>166.870</b> <b>±0.500</b>	<b>65.740</b> <b>±0.800</b>	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
HgO(montroydite, red) [1992GRE/FUG]	- 58.523 <sup>(a)</sup> ±0.154	- 90.790 ±0.120	70.250 ±0.300	
Hg <sub>2</sub> Cl <sub>2</sub> (cr) [1992GRE/FUG]	- 210.725 <sup>(a)</sup> ±0.471	- 265.370 ±0.400	191.600 ±0.800	
Hg <sub>2</sub> SO <sub>4</sub> (cr) [1992GRE/FUG]	- 625.780 <sup>(a)</sup> ±0.411	- 743.090 ±0.400	200.700 ±0.200	
Cu(cr) [1992GRE/FUG]	0.000	0.000	33.150 ±0.080	24.440 ±0.050
Cu(g) [1992GRE/FUG]	297.672 <sup>(a)</sup> ±1.200	337.400 ±1.200	166.398 ±0.004	20.786 ±0.001
Cu <sup>2+</sup> [1992GRE/FUG]	65.040 <sup>(a)</sup> ±1.557	64.900 ±1.000	- 98.000 ±4.000	
CuCl(g) [2003GUI/FAN]		76.800 ±10.000		
CuSO <sub>4</sub> (cr) [1992GRE/FUG]	- 662.185 <sup>(a)</sup> ±1.206	- 771.400 ±1.200	109.200 ±0.400	
Ag(cr) [1992GRE/FUG]	0.000	0.000	42.550 ±0.200	25.350 ±0.100
Ag(g) [1992GRE/FUG]	246.007 <sup>(a)</sup> ±0.802	284.900 ±0.800	172.997 ±0.004	20.786 ±0.001
Ag <sup>+</sup> [1992GRE/FUG]	77.096 <sup>(a)</sup> ±0.156	105.790 ±0.080	73.450 ±0.400	
AgCl(cr) [1992GRE/FUG]	- 109.765 <sup>(a)</sup> ±0.098	- 127.010 ±0.050	96.250 ±0.200	
Ni(cr) [2005GAM/BUG]	0.000 ±0.000	0.000 ±0.000	29.870 ±0.200	26.070 ±0.100
Ni <sup>2+</sup> [2005GAM/BUG]	- 45.773 ±0.771	- 55.012 <sup>(a)</sup> ±0.878	- 131.800 ±1.400	- 46.100 ±7.500
NiF <sub>2</sub> (cr) [2005GAM/BUG]	-609.852 <sup>(a)</sup> ±8.001	-657.300 ±8.000	73.520 ±0.400	63.210 ±2.000
Ti(cr) [1992GRE/FUG]	0.000	0.000	30.720 ±0.100	25.060 ±0.080
Ti(g) [1992GRE/FUG]	428.403 <sup>(a)</sup> ±3.000	473.000 ±3.000	180.298 ±0.010	24.430 ±0.030
TiO <sub>2</sub> (rutile) [1992GRE/FUG]	- 888.767 <sup>(a)</sup> ±0.806	- 944.000 ±0.800	50.620 ±0.300	55.080 ±0.300

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
TiCl <sub>4</sub> (g) [1992GRE/FUG]	- 726.324 <sup>(a)</sup> ±3.229	- 763.200 ±3.000	353.200 ±4.000	95.408 ±1.000
Am <sup>3+</sup> [1995SIL/BID]	-598.698 <sup>(a)</sup> ±4.755	-616.700 ±1.500	-201.000 ±15.000	
Pu <sup>3+</sup> [2001LEM/FUG]	-578.984 ±2.688	-591.790 ±1.964	-184.510 <sup>(b)</sup> ±6.154	
Np <sup>4+</sup> [2001LEM/FUG]	-491.774 <sup>(a)</sup> ±5.586	-556.022 ±4.185	-426.390 <sup>(b)</sup> ±12.386	
NpO <sub>2</sub> <sup>+</sup> [2001LEM/FUG]	-907.765 <sup>(a)</sup> ±5.628	-978.181 ±4.629	-45.904 ±10.706	-4.000 ±25.000
U(cr) [1992GRE/FUG]	0.000	0.000	50.200 ±0.200	27.660 ±0.050
U <sup>4+</sup> [2003GUI/FAN]	-529.860 <sup>(b)</sup> ±1.765	-591.200 ±3.300	-416.895 <sup>(a)</sup> ±12.553	-220.000 ±50.000
UO <sub>2</sub> <sup>2+</sup> [1992GRE/FUG]	-952.551 <sup>(a)</sup> ±1.747	-1019.000 ±1.500	-98.200 ±3.000	42.400 ±3.000
Be(cr) [1992GRE/FUG]	0.000	0.000	9.500 ±0.080	16.443 ±0.060
Be(g) [1992GRE/FUG]	286.202 <sup>(a)</sup> ±5.000	324.000 ±5.000	136.275 ±0.003	20.786 ±0.001
BeO(bromellite) [1992GRE/FUG]	- 580.090 <sup>(a)</sup> ±2.500	- 609.400 ±2.500	13.770 ±0.040	25.565 ±0.100
Mg(cr) [1992GRE/FUG]	0.000	0.000	32.670 ±0.100	24.869 ±0.020
Mg(g) [1992GRE/FUG]	112.521 <sup>(a)</sup> ±0.801	147.100 ±0.800	148.648 ±0.003	20.786 ±0.001
Mg <sup>2+</sup> [1992GRE/FUG]	- 455.375 <sup>(a)</sup> ±1.335	- 467.000 ±0.600	- 137.000 ±4.000	
MgO(cr) [1992GRE/FUG]	- 569.312 <sup>(a)</sup> ±0.305	- 601.600 ±0.300	26.950 ±0.150	37.237 ±0.200
MgF <sub>2</sub> (cr) [1992GRE/FUG]	- 1071.051 <sup>(a)</sup> ±1.210	- 1124.200 ±1.200	57.200 ±0.500	61.512 ±0.300
Ca(cr) [1992GRE/FUG]	0.000	0.000	41.590 ±0.400	25.929 ±0.300
Ca(g) [1992GRE/FUG]	144.021 <sup>(a)</sup> ±0.809	177.800 ±0.800	154.887 ±0.004	20.786 ±0.001

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Ca <sup>2+</sup> [1992GRE/FUG]	- 552.806 <sup>(a)</sup> ±1.050	- 543.000 ±1.000	- 56.200 ±1.000	
CaO(cr) [1992GRE/FUG]	- 603.296 <sup>(a)</sup> ±0.916	- 634.920 ±0.900	38.100 ±0.400	42.049 ±0.400
CaF(g) [2003GUI/FAN]	- 302.118 ±5.104	- 276.404 ±5.100	229.244 ±0.500	33.671 ±0.500
CaCl(g) [2003GUI/FAN]	- 129.787 ±5.001	- 103.400 ±5.000	241.634 ±0.300	35.687 ±0.010
Sr(cr) [1992GRE/FUG]	0.000	0.000	55.700 ±0.210	
Sr <sup>2+</sup> [1992GRE/FUG]	- 563.864 <sup>(a)</sup> ±0.781	- 550.900 ±0.500	- 31.500 ±2.000	
SrO(cr) [1992GRE/FUG]	- 559.939 <sup>(a)</sup> ±0.914	- 590.600 ±0.900	55.440 ±0.500	
SrCl <sub>2</sub> (cr) [1992GRE/FUG]	- 784.974 <sup>(a)</sup> ±0.714	- 833.850 ±0.700	114.850 ±0.420	
Sr(NO <sub>3</sub> ) <sub>2</sub> (cr) [1992GRE/FUG]	- 783.146 <sup>(a)</sup> ±1.018	- 982.360 ±0.800	194.600 ±2.100	
Ba(cr) [1992GRE/FUG]	0.000	0.000	62.420 ±0.840	
Ba(g) [2003GUI/FAN]	152.852 ±5.006	185.000 ±5.000	170.245 ±0.010	20.786 ±0.001
Ba <sup>2+</sup> [1992GRE/FUG]	- 557.656 <sup>(a)</sup> ±2.582	- 534.800 ±2.500	8.400 ±2.000	
BaO(cr) [1992GRE/FUG]	- 520.394 <sup>(a)</sup> ±2.515	- 548.100 ±2.500	72.070 ±0.380	
BaF(g) [2003GUI/FAN]	- 349.569 ±6.705	- 324.992 ±6.700	246.219 ±0.210	34.747 ±0.300
BaCl <sub>2</sub> (cr) [1992GRE/FUG]	- 806.953 <sup>(a)</sup> ±2.514	- 855.200 ±2.500	123.680 ±0.250	
Li(cr) [1992GRE/FUG]	0.000	0.000	29.120 ±0.200	24.860 ±0.200
Li(g) [1992GRE/FUG]	126.604 <sup>(a)</sup> ±1.002	159.300 ±1.000	138.782 ±0.010	20.786 ±0.001
Li <sup>+</sup> [1992GRE/FUG]	- 292.918 <sup>(a)</sup> ±0.109	- 278.470 ±0.080	12.240 ±0.150	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Na(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>51.300</b> <b>±0.200</b>	<b>28.230</b> <b>±0.200</b>
Na(g) [1992GRE/FUG]	<b>76.964</b> <sup>(a)</sup> <b>±0.703</b>	<b>107.500</b> <b>±0.700</b>	<b>153.718</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
Na <sup>+</sup> [1992GRE/FUG]	<b>-261.953</b> <sup>(a)</sup> <b>±0.096</b>	<b>-240.340</b> <b>±0.060</b>	<b>58.450</b> <b>±0.150</b>	
NaF(cr) [2001LEM/FUG]	<b>-546.327</b> <sup>(a)</sup> <b>±0.704</b>	<b>-576.600</b> <b>±0.700</b>	<b>51.160</b> <b>±0.150</b>	
NaCl(cr) [2001LEM/FUG]	<b>-384.221</b> <b>±0.147</b>	<b>-411.260</b> <b>±0.120</b>	<b>72.150</b> <b>±0.200</b>	<b>50.500</b>
NaNO <sub>3</sub> (cr) [2003GUI/FAN]		<b>-467.580</b> <b>±0.410</b>		
K(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>64.680</b> <b>±0.200</b>	<b>29.600</b> <b>±0.100</b>
K(g) [1992GRE/FUG]	<b>60.479</b> <sup>(a)</sup> <b>±0.802</b>	<b>89.000</b> <b>±0.800</b>	<b>160.341</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
K <sup>+</sup> [1992GRE/FUG]	<b>-282.510</b> <sup>(a)</sup> <b>±0.116</b>	<b>-252.140</b> <b>±0.080</b>	<b>101.200</b> <b>±0.200</b>	
KCl(cr) [2005GAM/BUG]		<b>-436.461</b> <b>±0.129</b>		
KBr(cr) [2005GAM/BUG]		<b>-393.330</b> <b>±0.188</b>		
KI(cr) [2005GAM/BUG]		<b>-329.150</b> <b>±0.137</b>		
Rb(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>76.780</b> <b>±0.300</b>	<b>31.060</b> <b>±0.100</b>
Rb(g) [1992GRE/FUG]	<b>53.078</b> <sup>(a)</sup> <b>±0.805</b>	<b>80.900</b> <b>±0.800</b>	<b>170.094</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
Rb <sup>+</sup> [1992GRE/FUG]	<b>-284.009</b> <sup>(a)</sup> <b>±0.153</b>	<b>-251.120</b> <b>±0.100</b>	<b>121.750</b> <b>±0.250</b>	
Cs(cr) [1992GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>85.230</b> <b>±0.400</b>	<b>32.210</b> <b>±0.200</b>
Cs(g) [1992GRE/FUG]	<b>49.556</b> <sup>(a)</sup> <b>±1.007</b>	<b>76.500</b> <b>±1.000</b>	<b>175.601</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
Cs <sup>+</sup> [1992GRE/FUG]	<b>-291.456</b> <sup>(a)</sup> <b>±0.535</b>	<b>-258.000</b> <b>±0.500</b>	<b>132.100</b> <b>±0.500</b>	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
CsCl(cr) [2001LEM/FUG]	- 413.807 <sup>(a)</sup> ±0.208	- 442.310 ±0.160	101.170 ±0.200	52.470
CsBr(cr) [2001LEM/FUG]	- 391.171 ±0.305	- 405.600 ±0.250	112.940 ±0.400	52.930

(a) Value calculated internally using  $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \sum S_{m,i}^\circ$ .

(b) Value calculated internally from reaction data (see Table IV-2).

Table IV-2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of thermodynamic data for the NEA TDB Project data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI of [1992GRE/FUG] and [2005OLI/NOL]. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Species and review where adopted	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
HF(aq) [1992GRE/FUG]	$F^- + H^+ \rightleftharpoons HF(aq)$ 3.180 ±0.020	$-18.152$ ±0.114	$12.200$ ±0.300	$101.800^{(a)}$ ±1.077
HF <sub>2</sub> <sup>-</sup> [1992GRE/FUG]	$F^- + HF(aq) \rightleftharpoons HF_2^-$ 0.440 ±0.120	$-2.511$ ±0.685	$3.000$ ±2.000	$18.486^{(a)}$ ±7.090
ClO <sup>-</sup> [2005OLI/NOL]	$HClO(aq) \rightleftharpoons ClO^- + H^+$ -7.420 ±0.130	$42.354$ ±0.742	$17.400$ ±2.100	$-83.695^{(a)}$ ±7.470
ClO <sub>2</sub> <sup>-</sup> [1992GRE/FUG]	$HClO_2(aq) \rightleftharpoons ClO_2^- + H^+$ -1.960 ±0.020	$11.188$ ±0.114		
HClO(aq) [1992GRE/FUG]	$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^- + H^+ + HClO(aq)$ -4.537 ±0.105	$25.900$ ±0.600		
HClO <sub>2</sub> (aq) [1992GRE/FUG]	$H_2O(l) + HClO(aq) \rightleftharpoons 2H^+ + HClO_2(aq) + 2e^-$ -55.400 <sup>(b)</sup> ±0.700	$316.230$ ±3.996		
BrO <sup>-</sup> [1992GRE/FUG]	$HBrO(aq) \rightleftharpoons BrO^- + H^+$ -8.630 ±0.030	$49.260$ ±0.171	$30.000$ ±3.000	$-64.600^{(a)}$ ±10.078
HBrO(aq) [1992GRE/FUG]	$Br_2(aq) + H_2O(l) \rightleftharpoons Br^- + H^+ + HBrO(aq)$ -8.240 ±0.200	$47.034$ ±1.142		

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Table IV-2 (continued)

Species and review where adopted	$\log_{10} K^{\circ}$	Reaction		
		$\Delta_r G_m^{\circ}$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^{\circ}$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^{\circ}$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
HIO <sub>3</sub> (aq) [1992GRE/FUG]	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$ 0.788 ±0.029	-4.498 ±0.166		
S <sup>2-</sup> [1992GRE/FUG]	$HS^- \rightleftharpoons H^+ + S^{2-}$ -19.000 ±2.000	108.450 ±11.416		
SO <sub>3</sub> <sup>2-</sup> [1992GRE/FUG]	$H_2O(l) + SO_4^{2-} + 2 e^- \rightleftharpoons 2OH^- + SO_3^{2-}$ -31.400 <sup>(b)</sup> ±0.700	179.230 ±3.996		
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> [1992GRE/FUG]	$3H_2O(l) + 2SO_3^{2-} + 4 e^- \rightleftharpoons 6OH^- + S_2O_3^{2-}$ -39.200 <sup>(b)</sup> ±1.400	223.760 ±7.991		
H <sub>2</sub> S(aq) [1992GRE/FUG]	$H_2S(aq) \rightleftharpoons H^+ + HS^-$ -6.990 ±0.170	39.899 ±0.970		
HSO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$ 7.220 ±0.080	-41.212 ±0.457	66.000 ±30.000	359.590 <sup>(a)</sup> ±100.630
HS <sub>2</sub> O <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$ 1.590 ±0.150	-9.076 ±0.856		
H <sub>2</sub> SO <sub>3</sub> (aq) [1992GRE/FUG]	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$ 1.840 ±0.080	-10.503 ±0.457	16.000 ±5.000	88.891 <sup>(a)</sup> ±16.840
HSO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ 1.980 ±0.050	-11.302 ±0.285		
Se(g) [2005OLI/NOL]	$0.5Se_2(g) \rightleftharpoons Se(g)$		-165.520 ±0.250	
Se <sup>2-</sup> [2005OLI/NOL]	$Se(cr) + 2 e^- \rightleftharpoons Se^{2-}$ -22.530 ±0.526	128.600 ±3.000		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^{\circ}$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^{\circ}$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Se <sub>2</sub> <sup>2-</sup> [2005OLI/NOL]	$2\text{Se}^{2-} \rightleftharpoons \text{Se}_2^{2-} + 2\text{e}^-$ 25.320 ±0.333	-144.530 ±1.900		
Se <sub>3</sub> <sup>2-</sup> [2005OLI/NOL]	$3\text{Se}^{2-} \rightleftharpoons \text{Se}_3^{2-} + 4\text{e}^-$ 49.966 ±0.333	-285.210 ±1.900		
Se <sub>4</sub> <sup>2-</sup> [2005OLI/NOL]	$4\text{Se}^{2-} \rightleftharpoons \text{Se}_4^{2-} + 6\text{e}^-$ 73.023 ±0.333	-416.820 ±1.900		
SeO <sub>2</sub> (g) [2005OLI/NOL]	$\text{SeO}_2(\text{cr}) \rightleftharpoons \text{SeO}_2(\text{g})$		114.800 ±2.500	
SeO <sub>3</sub> <sup>2-</sup> [2005OLI/NOL]	$\text{HSeO}_3^- \rightleftharpoons \text{H}^+ + \text{SeO}_3^{2-}$ -8.360 ±0.230	47.719 ±1.313		
SeO <sub>4</sub> <sup>2-</sup> [2005OLI/NOL]	$\text{HSeO}_4^- \rightleftharpoons \text{H}^+ + \text{SeO}_4^{2-}$ -1.750 ±0.100	-9.989 ±0.571	-20.800 ±3.200	-103.267 <sup>(a)</sup> ±10.902
Se <sub>2</sub> O <sub>5</sub> (cr) [2005OLI/NOL]	$\text{SeO}_2(\text{cr}) + \text{SeO}_3(\text{cr}) \rightleftharpoons \text{Se}_2\text{O}_5(\text{cr})$		-26.100 ±1.200	
HSe <sup>-</sup> [2005OLI/NOL]	$\text{H}_2\text{Se}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HSe}^-$ -3.850 ±0.050	21.976 ±0.285		
H <sub>2</sub> Se(aq) [2005OLI/NOL]	$\text{H}_2\text{Se}(\text{g}) \rightleftharpoons \text{H}_2\text{Se}(\text{aq})$ -1.100 ±0.010	6.279 ±0.057	-14.700 ±0.300	-70.363 <sup>(a)</sup> ±1.024
HSeO <sub>3</sub> <sup>-</sup> [2005OLI/NOL]	$\text{H}_2\text{SeO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HSeO}_3^-$ -2.640 ±0.140	15.069 ±0.799		
HSeO <sub>4</sub> <sup>-</sup> [2005OLI/NOL]	$\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{SeO}_3(\text{aq}) \rightleftharpoons 3\text{H}^+ + \text{HSeO}_4^- + 2\text{e}^-$ -37.289 <sup>(c)</sup> ±0.175	212.847 ±1.000		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
H <sub>2</sub> SeO <sub>3</sub> (cr) [2005OLI/NOL]	H <sub>2</sub> O(l) + SeO <sub>2</sub> (cr) ⇌ H <sub>2</sub> SeO <sub>3</sub> (cr)		-13.500 ±0.180	
H <sub>2</sub> SeO <sub>3</sub> (aq) [2005OLI/NOL]	3H <sub>2</sub> O(l) + Se(cr) ⇌ 2H <sub>2</sub> (g) + H <sub>2</sub> SeO <sub>3</sub> (aq)	-50.147 ±0.147	286.240 ±0.840	
HN <sub>3</sub> (aq) [1992GRE/FUG]	H <sup>+</sup> + N <sub>3</sub> <sup>-</sup> ⇌ HN <sub>3</sub> (aq)	4.700 ±0.080	-26.828 ±0.457	-15.000 ±10.000
NH <sub>3</sub> (aq) [1992GRE/FUG]	NH <sub>4</sub> <sup>+</sup> ⇌ H <sup>+</sup> + NH <sub>3</sub> (aq)	-9.237 ±0.022	52.725 ±0.126	52.090 ±0.210
HNO <sub>2</sub> (aq) [1992GRE/FUG]	H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> ⇌ HNO <sub>2</sub> (aq)	3.210 ±0.160	-18.323 ±0.913	-11.400 ±3.000
PO <sub>4</sub> <sup>3-</sup> [1992GRE/FUG]	HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup>	-12.350 ±0.030	70.494 ±0.171	14.600 ±3.800
P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> [1992GRE/FUG]	HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> ⇌ H <sup>+</sup> + P <sub>2</sub> O <sub>7</sub> <sup>4-</sup>	-9.400 ±0.150	53.656 ±0.856	
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> [1992GRE/FUG]	H <sup>+</sup> + HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.212 ±0.013	-41.166 ±0.074	-3.600 ±1.000
H <sub>3</sub> PO <sub>4</sub> (aq) [1992GRE/FUG]	H <sup>+</sup> + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ⇌ H <sub>3</sub> PO <sub>4</sub> (aq)	2.140 ±0.030	-12.215 ±0.171	8.480 ±0.600
HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> [1992GRE/FUG]	H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup>	-6.650 ±0.100	37.958 ±0.571	
H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> [1992GRE/FUG]	H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> ⇌ H <sup>+</sup> + H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	-2.250 ±0.150	12.843 ±0.856	

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> [1992GRE/FUG]	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) ⇌ H <sup>+</sup> + H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> - 1.000 ±0.500	5.708 ±2.854		
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) [1992GRE/FUG]	2H <sub>3</sub> PO <sub>4</sub> (aq) ⇌ H <sub>2</sub> O(l) + H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) - 2.790 ±0.170	15.925 ±0.970	22.200 ±1.000	21.045 <sup>(a)</sup> ±4.673
CO <sub>2</sub> (aq) [1992GRE/FUG]	H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup> ⇌ CO <sub>2</sub> (aq) + H <sub>2</sub> O(l) 6.354 ±0.020	- 36.269 ±0.114		
CO <sub>2</sub> (g) [1992GRE/FUG]	CO <sub>2</sub> (aq) ⇌ CO <sub>2</sub> (g) 1.472 ±0.020	- 8.402 ±0.114		
HCO <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup> ⇌ HCO <sub>3</sub> <sup>-</sup> 10.329 ±0.020	- 58.958 ±0.114		
CN <sup>-</sup> [2005OLI/NOL]	HCN(aq) ⇌ CN <sup>-</sup> + H <sup>+</sup> - 9.210 ±0.020	52.571 ±0.114	43.600 ±0.200	- 30.089 <sup>(a)</sup> ±0.772
HCN(aq) [2005OLI/NOL]	HCN(g) ⇌ HCN(aq) 0.902 ±0.050	- 5.149 ±0.285	- 26.150 ±2.500	- 70.439 <sup>(a)</sup> ±8.440
SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> [1992GRE/FUG]	Si(OH) <sub>4</sub> (aq) ⇌ 2H <sup>+</sup> + SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> - 23.140 ±0.090	132.080 ±0.514	75.000 ±15.000	- 191.460 <sup>(a)</sup> ±50.340
SiO(OH) <sub>3</sub> <sup>-</sup> [1992GRE/FUG]	Si(OH) <sub>4</sub> (aq) ⇌ H <sup>+</sup> + SiO(OH) <sub>3</sub> <sup>-</sup> - 9.810 ±0.020	55.996 ±0.114	25.600 ±2.000	- 101.950 <sup>(a)</sup> ±6.719
Si(OH) <sub>4</sub> (aq) [1992GRE/FUG]	2H <sub>2</sub> O(l) + SiO <sub>2</sub> (α-quartz) ⇌ Si(OH) <sub>4</sub> (aq) - 4.000 ±0.100	22.832 ±0.571	25.400 ±3.000	8.613 <sup>(a)</sup> ±10.243
Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>2-</sup> [1992GRE/FUG]	2Si(OH) <sub>4</sub> (aq) ⇌ 2H <sup>+</sup> + H <sub>2</sub> O(l) + Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>2-</sup> - 19.000 ±0.300	108.450 ±1.712		

(Continued on next page)

Table IV-2 (continued)

Species and review where adopted	$\log_{10} K^\circ$	Reaction		
		$\Delta_r G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_r S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>-</sup> [1992GRE/FUG]	2Si(OH) <sub>4</sub> (aq) ⇌ H <sup>+</sup> + H <sub>2</sub> O(l) + Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>-</sup>	- 8.100 ±0.300	46.235 ±1.712	
Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3-</sup> [1992GRE/FUG]	3Si(OH) <sub>4</sub> (aq) ⇌ 3H <sup>+</sup> + 3H <sub>2</sub> O(l) + Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3-</sup>	- 28.600 ±0.300	163.250 ±1.712	
Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3-</sup> [1992GRE/FUG]	3Si(OH) <sub>4</sub> (aq) ⇌ 3H <sup>+</sup> + 2H <sub>2</sub> O(l) + Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3-</sup>	- 27.500 ±0.300	156.970 ±1.712	
Si <sub>4</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4-</sup> [1992GRE/FUG]	4Si(OH) <sub>4</sub> (aq) ⇌ 4H <sup>+</sup> + 4H <sub>2</sub> O(l) + Si <sub>4</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4-</sup>	- 36.300 ±0.500	207.200 ±2.854	
Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3-</sup> [1992GRE/FUG]	4Si(OH) <sub>4</sub> (aq) ⇌ 3H <sup>+</sup> + 4H <sub>2</sub> O(l) + Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3-</sup>	- 25.500 ±0.300	145.560 ±1.712	

(a) Value calculated internally using  $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \Delta_r S_m^\circ$ .

(b) Value calculated from a selected standard potential.

## **Part 3**

### **Discussion of data selection**



# Chapter V

## Elemental tin

### V.1 Tin crystal

#### V.1.1 General considerations

Solid tin exists in two forms. The low-temperature cubic modification (also called  $\alpha$ -Sn or “grey” tin) transforms to a tetragonal solid (also called  $\beta$ -Sn or “white” tin). Both the temperature and enthalpy of transformation are somewhat uncertain because the transition is sluggish.  $\beta$ -Sn can be supercooled to very low temperatures.

Cohen and coworkers carried out early measurements of the  $\alpha \rightarrow \beta$  transition temperature [1899COH/EIJ], [1908COH], [1927COH/DEK], [1935COH/LIE] using electrical and dilatometric methods. They reported temperatures between 285 and 293 K, the most reliable being  $T_{\text{trs}} = (286.35 \pm 0.10)$  K [1935COH/LIE]. The careful and systematic experiments of Raynor *et al.* [1958RAY/SMI] by dilatometry showed that the transition temperature was significantly influenced by the state of the white tin in the sample. They reported a transition temperature for strain-free Sn of  $(283.55 \pm 0.45)$  K and  $(286.5 \pm 0.3)$  K for strained Sn. In compilations/evaluations, Hultgren *et al.* [1963HUL/ORR] and [1973HUL/DES] recommend  $(286.2 \pm 3.0)$  and  $(286.2 \pm 0.5)$  K, respectively, while Gurvich *et al.* [1991GUR/VEY] states 287 K without further discussion or qualification. The selected value for the present evaluation has been obtained from the value for strain-free tin [1958RAY/SMI] and the one of [1935COH/LIE] by the method described in example C.2 (see Appendix C):

$$T_{\text{trs}} = (285 \pm 2) \text{ K.}$$

There is thought to be evidence of a transition in white tin between 420 and 470 K. Bartenev [1947BAR] found an anomaly in the heat capacity-temperature curve at about 440 K. This was corroborated by Klemm and Niermann [1963KLE/NIE], who observed a slight, abrupt discontinuity in the enthalpy curve ( $\approx 200 \text{ J}\cdot\text{mol}^{-1}$ ) at about 448 K. Klemm and Niermann [1963KLE/NIE] also presented data showing a discontinuity in the temperature dependence of the  $a$ -axis lattice parameter of tetragonal tin (the  $c$ -axis showed no such discontinuity). The temperature dependence of the electrical conductivity showed (less convincing) anomalies at about the same temperature. These observations were later discussed by Grønvold [1974GRO], whose very careful adiabatic calorimetric  $C_{p,m}^{\circ}$  measurements showed no discontinuity. This

transition, called “second order” by Klemm and Niermann [1963KLE/NIE], will not be considered further in the present evaluation.

The melting point of tin has been accurately measured, and the adopted value is  $(505.118 \pm 0.015)$  K on the 1968-IPTS basis [1973HUL/DES2], [1991GUR/VEY].

### V.1.2 Properties of grey tin

Low-temperature measurements of the heat capacity were obtained by adiabatic calorimetry ([1924LAN]: 16 to 103 K, and 284 K; [1952HIL/PAR]: 7 to 100 K and [1955WEB/WIL]: 1.5 to 4 K). Kelley and King [1961KEL/KIN] interpolated values between 103 and 298 K. Twenty values given by [1973HUL/DES] were used to derive the standard entropy (see Table V-1).

The enthalpy of the  $\alpha \rightarrow \beta$  transition,  $\Delta_{\alpha}^{\beta}H_{\text{Sn}}^{*}$ , was determined by calorimetry by [1914BRO] ( $2.23 \text{ kJ}\cdot\text{mol}^{-1}$ ) and by measuring the temperature dependence of the potential of the cell



( $3.05 \text{ kJ}\cdot\text{mol}^{-1}$ ) [1899COH/EIJ], [1899COH]. Although the electrochemical cell consisting of the stable and metastable tin phase connected by an aqueous hexachlorido stannate solution looked promising, it turned out that it did not provide reliable values for  $\Delta_{\alpha}^{\beta}H_{\text{Sn}}^{*}$  [1914BRO]. Hultgren *et al.* [1973HUL/DES] reported a value of  $(1.97 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}$  from third law integration.

Table V-1: Properties of grey tin as given in compilations/evaluations.

Reference	$\Delta_f H_m^{\circ}$ (Sn, $\alpha$ , 298.15 K)/ $\text{kJ}\cdot\text{mol}^{-1}$	$S_m^{\circ}$ (Sn, $\alpha$ , 298.15 K)/ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$C_{p,m}^{\circ}$ (Sn, $\alpha$ , 298.15 K)/ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
[1952ROS/WAG]	- 2.5	44.14	25.77
[1973HUL/DES]	- 1.98	$44.14 \pm 0.42$	25.8
[1982WAG/EVA]		44.14	25.77

Since both the temperature and enthalpy of the  $\alpha \rightarrow \beta$  transition are uncertain, the heat capacity and derived standard entropy are considered to be better established than the standard enthalpy of formation of  $\alpha$ -Sn. The following selected data and uncertainties assigned are from [1973HUL/DES]:

$$C_{p,m}^{\circ} (\text{Sn}, \alpha, 298.15 \text{ K}) = (25.8 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m^{\circ} (\text{Sn}, \alpha, 298.15 \text{ K}) = (44.14 \pm 0.42) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$\Delta_f H_m^{\circ} (\text{Sn}, \alpha, 298.15 \text{ K}) = - (1.98 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}.$$

With  $C_{p,m}^{\circ}(\text{Sn}, \beta, 298.15 \text{ K}) = (27.11 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , see Section V.1.3,  $\Delta_f G_m^{\circ}(\text{Sn}, \alpha, 298.15 \text{ K})$  can be calculated:

$$\Delta_f G_m^{\circ}(\text{Sn}, \alpha, 298.15 \text{ K}) = (0.12 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}.$$

### V.1.3 Properties of white tin

Information on original data sources is given in Table V-2. Although the data of Chen and Turnbull [1968CHE/TUR], in the publication, are given only as points on a diagram, it is possible that later evaluators [1973HUL/DES2], [1991GUR/VEY] may have had access to tabulated data.

Table V-2: Heat capacity of white tin. Information on original data sources.

Reference	Number of data points	$T/\text{K}$	Comments *
[1849PER]	1	505	
[1904TIL]	2	373, 423	
[1910SCH2]	5	123 – 323	
[1914SCH]	2	323, 373	
[1919IIT]	18	356 – 505	
[1926AWB/GRI]	4	366 – 505	Only heat content reported.
[1926UMI]	7	323 – 498	
[1927KLI]	10	325 – 500	Adiabatic calorimetry. Heating by thermionic electrons. Points on graph only.
[1932JAE/BOT]	8	273 – 505	
[1960GEN/HAG]	3	481 – 505	Adiabatic calorimetry. Only heat content reported.
[1963KLE/NIE]	21	382 – 488	Points on graph only.
[1966YAM/HEA]	2	350, 450	
[1968CHE/TUR]	≈ 85	327 – 505	DSC. Data on graph only.
[1974GRO]	40	300 – 505	Adiabatic calorimetry
[1979NAU/NOG]	108	1.7 – 311	Adiabatic calorimetry

\* Unless otherwise stated, the experimental method used was drop calorimetry (method of mixtures).

The results of accepted  $C_{p,m}^{\circ}(\text{Sn}, \beta, T)$  measurements are given in Table V-3, together with the values of the evaluation selected at present, see [1991GUR/VEY] (reasons for this choice are given below). Similarly, experimental heat content data are compared with the selected data in Table V-4.

Table V-3: Comparison of  $C_{p,m}^{\circ}$  (Sn,  $\beta$ ,  $T$ ) measurements of white tin with selected reference data [1991GUR/VEY]\*.

$T/K$	$C_{p,m}^{\circ}$ (Sn, $\beta$ , $T$ )/J·K <sup>-1</sup> ·mol <sup>-1</sup>		
	Reference	Experiment Value	Selected [1991GUR/VEY]
298.15	[1974GRO]	27.10	27.112
	[1979NAU/NOG]	27.00	
	[1919IIT]	26.01	
300	[1932JAE/BOT]	26.83	27.147
	[1974GRO]	27.14	
323	[1914SCH]	27.6	27.561
	[1919IIT]	26.82	
	[1932JAE/BOT]	27.39	
350	[1966YAM/HEA]	27.95	28.025
373	[1914SCH]	28.5	28.421
	[1919IIT]	28.50	
	[1932JAE/BOT]	28.11	
400	[1974GRO]	28.89	28.903
423	[1919IIT]	30.10	29.338
	[1932JAE/BOT]	28.95	
450	[1966YAM/HEA]	30.63	29.887
473	[1932JAE/BOT]	29.89	30.391
500	[1974GRO]	31.47	31.033
$T_{\text{fus}}$	[1974GRO]	31.69	31.16
	[1919IIT]	32.9	
	[1932JAE/BOT]	30.56	

\* The number of significant figures in this table are those of the original experimenter/evaluator.

In Table V-3 and Table V-4, the heat-capacity and enthalpy values at  $T_{\text{fus}}$  are extrapolated values. Since, at the phase change temperature  $T_{\text{fus}}$ , both enthalpy and heat capacity are considered to be discontinuous functions, the quantities are undefined at that temperature, or approach infinity, as the accurate measurements of Grønvold [1974GRO] show.



Table V-4: Comparison of experimental enthalpy differences of white tin with selected reference data [1991GUR/VEY2].

T/K	$H_m(\text{Sn}, \beta, T) - H_m(\text{Sn}, \beta, 471 \text{ K})/\text{J}\cdot\text{mol}^{-1}$	
	[1960GEN/HAG]	[1991GUR/VEY2]
481	289	303
491	573	609
$T_{\text{fus}}$	1004	1044
T/K	$H_m(\text{Sn}, \beta, T) - H_m(\text{Sn}, \beta, 291 \text{ K})/\text{J}\cdot\text{mol}^{-1}$	
	[1926AWB/GRI]	[1991GUR/VEY2]
366	2210	2075
421	3623	3664
453	4594	4614
$T_{\text{fus}}$	6094	6201

Table V-5 lists compilations/evaluations which present data as a function of temperature. The compilations [1952ROS/WAG], [1968WAG/EVA] and [1982WAG/EVA] include data only at 298.15 K. Some references in Table V-5 contain fitting equations, the parameters of which are found in Table V-6. The equation of Jaeger and Bottema [1932JAE/BOT] is a fitting equation for the authors' own experimental measurements only, and is given here for comparison.

Table V-5: Survey of compilations/evaluations of the heat capacity of white tin  $C_{p,m}^{\circ}(\text{Sn}, \beta, T)$ .

Reference	T/K	Discussion	Data source given
[1956STU/SIN]	298 – 505	N	Y
[1960KEL]	350 – 505	N	Y
[1963HUL/ORR], [1973HUL/DES]	298 – 505	Y	Y
[1973BAR/KNA]			
[1973HUL/DES2], [1982PAN], [1993BAR], [1991DIN]	298 – 505	Y	Y
[1978ROB/HEM]	298 – 505	N	Y
[1991GUR/VEY], [1993MCB/GOR], [1995ROB/HEM]	100 – 505	Y	Y
[1999BIN/MIL]	298 – 505	N	N

Table V-6: Parameters of fitting equations for the heat capacity of white tin  $C_{p,m}^o(\text{Sn}, \beta, T)/\text{J}\cdot\text{K}^{-1}\text{mol}^{-1} = a + b T/\text{K} + c (T/\text{K})^2 + d (T/\text{K})^{-2} + e (T/\text{K})^{-0.5}$ .

Reference	$a$	$b$	$c$	$d$	$e$	$T/\text{K}$
[1932JAE/BOT]	25.432	$-1.171 \times 10^{-3}$	0	0	$2.2404 \times 10^{-5}$	273 – 505
[1960KEL]	18.5	$2.64 \times 10^{-2}$	0	0	0	350 – 505
[1978ROB/HEM]	0	$5.0767 \times 10^{-2}$	$-2.3035 \times 10^{-5}$	$-6.0419 \times 10^4$	251.75	298 – 505
[1991GUR/VEY]	34.297	$-2.9957 \times 10^{-2}$	$5.0794 \times 10^{-5}$	$-2.461 \times 10^5$	0	298 – 505
[1999BIN/MIL]	21.59	$1.816 \times 10^{-2}$	0	0	0	298 – 505

The discussion and references to data sources from both [1973HUL/DES2] and [1991GUR/VEY] are given in Table V-5. The preferred data of both these evaluations are [1926AWB/GRI], [1932JAE/BOT], [1968CHE/TUR], and [1960GEN/HAG] with further addition of [1974GRO]. For present purposes, [1991GUR/VEY] provided a source of evaluated data which qualified for selection.

The standard, or third law, entropy is most accurately found from an integration of the heat capacity in the interval  $0 < T/\text{K} < 298$ . Early measurements ([1923ROD], [1924LAN], [1932KEE/KOK], [1932KEE/END], [1936KEE/LAE], [1937KEE/LAE], [1938KEE/LAE], [1952HIL/PAR], [1955WEB/WIL], [1956COR/SAT], [1957GOO], [1957ZAV], [1961BRY/KEE], [1965ONE/PHI], [1969CET/HOL]) covered the range 0 to 280 K for normal and superconducting tin. The method used was adiabatic calorimetry (in [1957ZAV],  $C_{p,m}^o(\text{Sn}, \beta, T)$  was derived from measurements of thermal conductivity). In a later study, Naumov *et al.* [1979NAU/NOG], made 105 measurements also using adiabatic calorimetry between 1 and 283 K.

Table V-7 contains various values of the standard entropy of white tin from compilations/evaluations.

Table V-7: The standard entropy of white tin as recommended in compilations/evaluations.

Reference	$S_m^o(\text{Sn}, \beta, 298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$
[1978COX], [1991GUR/VEY]	$51.18 \pm 0.08$
[1973HUL/DES], [1973BAR/KNA], [1993BAR]	$51.20 \pm 0.42$
[1978ROB/HEM], [1999BIN/MIL]	$51.20 \pm 0.42$
[1956STU/SIN]	51.42
[1952ROS/WAG]	51.5
[1963HUL/ORR], [1968WAG/EVA], [1982WAG/EVA]	$51.55 \pm 0.25$

For white tin, the enthalpy difference ( $H_m(\text{Sn}, \beta, 298.15 \text{ K}) - H_m(\text{Sn}, \beta, 0 \text{ K})$ ), as derived from the selected equation for  $C_{p,m}^o(\text{Sn}, \beta, T)$  (Table V-6), the original evaluators [1991GUR/VEY] assigned an uncertainty of  $\pm 0.08 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . They similarly assigned an uncertainty in  $C_{p,m}^o(\text{Sn}, \beta, 298.15 \text{ K})$  of  $0.08 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

From Table V-7, it may be concluded that a low, rather than a high, value of  $S_m^o(\text{Sn}, \beta, 298.15 \text{ K})$  is preferable. The present evaluation therefore selects that of [1991GUR/VEY], which corresponds to the value chosen by CODATA [1989COX/WAG].

The selected data for the heat capacity of white tin [1991GUR/VEY] are for  $298 < T/\text{K} < 505$  generated by the equation:

$$[C_{p,m}^o]_{298\text{K}}^{505\text{K}}(\text{Sn}, \beta, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 34.297 - 2.9957 \times 10^{-2} T/\text{K} \\ + 5.0794 \times 10^{-5} (T/\text{K})^2 - 2.461 \times 10^{-5} (T/\text{K})^{-2}$$

$$C_{p,m}^o(\text{Sn}, \beta, 298.15 \text{ K}) = (27.11 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and for the standard entropy the value

$$S_m^o(\text{Sn}, \beta, 298.15 \text{ K}) = (51.18 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

has been selected.



# Chapter VI

## Simple tin aqua ions

### VI.1 Preliminary remarks

The standard Gibbs energies of formation of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  have been determined by potentiometric measurements. In this review the SIT approach, see Appendix B, was used to extrapolate experimental equilibrium data to zero ionic strength. Activity coefficients in general and the SIT method in particular are based on molality as composition variable. Thus amount concentration, used in the literature, had to be converted to molality. For a comprehensive list of formulae for conversion see [2003LOR].

In this context it is convenient to define formal potentials  $E_c^{\circ'}$  and  $E_m^{\circ'}$  on concentration and molality bases, respectively.

$$E_c^{\circ'} = E + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10}(c_i/c^\circ) \quad \text{Eq. (II.34)}$$

$$E_m^{\circ'} = E + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10}(m_i/m^\circ) \quad \text{(VI.1)}$$

$$E_m^{\circ'} = E_c^{\circ'} + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10} \left( \frac{m_i/m^\circ}{c_i/c^\circ} \right) \quad \text{(VI.2)}$$

Equation (VI.2) shows that the definitions of  $E_m^{\circ'}$  and  $E_c^{\circ'}$  parallel exactly those of  $\log_{10} K_m$  and  $\log_{10} K_c$ , see Eq. (II.37).

$$E_c^\circ = E_c^{\circ'} + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10} \gamma_{c,i} = - \left( \frac{\Delta_r G_m^\circ}{nF} \right)_c \quad \text{(VI.3)}$$

$$E_m^\circ = E_m^{\circ'} + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10} \gamma_{m,i} = - \left( \frac{\Delta_r G_m^\circ}{nF} \right)_m \quad \text{(VI.4)}$$

$$\gamma_{c,i} = \left( \frac{m_i/m^\circ}{c_i/c^\circ} \right) (\rho_{\text{H}_2\text{O}}^*/\rho^\circ) \gamma_{m,i} \quad \text{Eq. (II.35c)}$$

$$E_c^\circ = E_c^{\circ'} + \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10} \left( \frac{m_i \rho_{\text{H}_2\text{O}}^* \gamma_{m,i}}{c_i} \right) = - \left( \frac{\Delta_r G_m^\circ}{nF} \right)_c \quad \text{Eq. (II.35b)}$$

The numerical error caused by omitting the density of pure solvent water  $\rho_{\text{H}_2\text{O}}^*$  is at least at ambient temperatures essentially negligible. Subtracting Eq. (II.35b) from Eq. (VI.4) results in Eq. (VI.5)

$$E_m^\circ = E_c^\circ - \left( \frac{RT \ln(10)}{nF} \right) \sum \nu_i \log_{10}(\rho_{\text{H}_2\text{O}}^*/\rho^\circ) \quad (\text{VI.5})$$

where  $\rho_{\text{H}_2\text{O}}^*$  is the density of pure water and  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$ ,  $c^\circ = 1 \text{ mol}\cdot\text{dm}^{-3}$  and  $\rho^\circ = 1 \text{ kg}\cdot\text{dm}^{-3}$ .

As  $(RT \ln(10)/nF) \sum \nu_i \log_{10}(\rho_{\text{H}_2\text{O}}^*/\rho^\circ) \approx 0$ , it follows from Eq. (VI.5) that  $E_m^\circ \approx E_c^\circ$  and  $(\Delta_r G_m^\circ)_m \approx (\Delta_r G_m^\circ)_c$ . The equality of these quantities is in fact tacitly assumed throughout the TDB volumes on Chemical Thermodynamics.

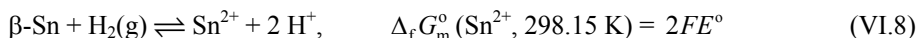
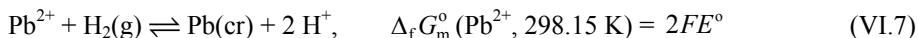
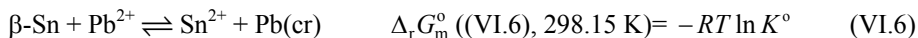
For this review standard electrode potentials were evaluated by converting the concentrations of background electrolyte and potential determining ions to molalities and plotting and regressing  $E_m^{\circ'}$  plus the appropriate Debye-Hückel term versus molality of the ion leading to specific short range interactions.

## VI.2 Sn<sup>2+</sup>

Although the basic thermodynamic data of Sn<sup>2+</sup> are listed as CODATA key values [1989COX/WAG], it was decided to re-evaluate these quantities for this review.

### VI.2.1 Gibbs energy of formation of Sn<sup>2+</sup>

The Gibbs energy of formation of Sn<sup>2+</sup>,  $\Delta_r G_m^\circ(\text{Sn}^{2+})$ , according to Reaction (VI.8) can be determined by combining Reactions (VI.6) and (VI.7).

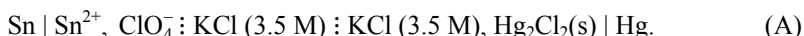


Noyes and Toabe [1917NOY/TOA] determined the equilibrium constant of Reaction (VI.6) in aqueous HClO<sub>4</sub>-Sn(ClO<sub>4</sub>)<sub>2</sub>-Pb(ClO<sub>4</sub>)<sub>2</sub> solutions at 25 °C. Equilibrium was attained from both sides within 10 to 19 days. The mean values of 11 independent measurements were  $m_{\text{Sn}^{2+}}/m_{\text{Pb}^{2+}} = (2.98 \pm 0.02)$ ,  $[E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Pb}^{2+}/\text{Pb}(0))] = -(14.0 \pm 0.1) \text{ mV}$ . For details, see Appendix A. In order to obtain the recalculated value,  $\Delta_r G_m^\circ(\text{Sn}^{2+}) = -(26.99 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$ , the CODATA key value of  $\Delta_r G_m^\circ(\text{Pb}^{2+}, 298.15 \text{ K}) = -(24.20 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$  [1989COX/WAG] was accepted.

Prytz [1928PRY] determined the standard half-cell potential for Reaction (VI.9)



at 24.5 °C in aqueous perchlorate solutions using the cell:



The critical evaluation of [1999LOT/OCH] and [2002HUM/BER] was based on these data. The original mean value of  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 297.65 \text{ K}) = -(26.17 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$  deviates by  $1.43 \text{ kJ}\cdot\text{mol}^{-1}$  from the value recommended by CODATA ( $-(27.60 \pm 0.40) \text{ kJ}\cdot\text{mol}^{-1}$ ) [1989COX/WAG]. In the course of the re-evaluation of these data the potential of the 3.5 M KCl calomel electrode vs. SHE at 24.5 °C must be taken into account. The value used by Prytz [1928PRY],  $E^\circ(3.5 \text{ M KCl, calomel, } 24.5 \text{ }^\circ\text{C}) = (250.5 \pm 1.0) \text{ mV}$ , was accepted for the SIT recalculation. For comparison with  $E^\circ$  values determined at 298.15 K a minor correction was applied based on  $S_m^\circ(\text{Sn}^{2+})$  selected in this review, which resulted in  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 298.15 \text{ K}) = -(133.54 \pm 3.00) \text{ mV}$  and  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(25.77 \pm 0.58) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. Thus a value of  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 297.65 \text{ K}) = -(133.7 \pm 3.0) \text{ mV}$  was obtained. The main part of the difference between this value and the one arrived at by [1999LOT/OCH] and [2002HUM/BER] is due to the potential of the calomel electrode (saturated KCl) vs. SHE, which was erroneously used by the latter.

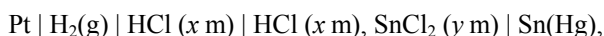
Haring and White [1938HAR/WHI] determined the standard potential of Reaction (VI.10):



at 25 °C by measuring the potential of cells of the types:

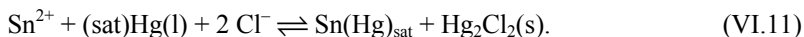


and



where  $x = 100y$ . The experimental cell-potential data were re-analysed taking  $\varepsilon(\text{H}^+, \text{Cl}^-)$  from NEA TDB auxiliary data (Table B-4) and  $\varepsilon(\text{Sn}^{2+}, \text{Cl}^-)$  as well as chlorido complex formation constants from this review. A standard potential  $E^\circ(\text{Sn}^{2+}/\text{Sn}(\text{Hg})_{\text{sat}}, 298.15 \text{ K}) = -(140.97 \pm 0.65) \text{ mV}$  was obtained (see Figure A-13). With the activity of tin in a saturated amalgam,  $a_{\text{Sn}} = 0.927$ , given by [2003YEN/GRO] this results in  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.02 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$ .

Riccoboni *et al.* [1949RIC/POP] determined polarographically the half-wave potential of  $\text{Sn}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Sn}(0)$  vs. the normal calomel electrode leading to the standard potential of Reaction (VI.11)

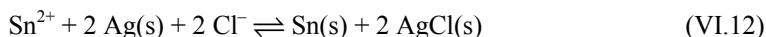


With a value for  $\varepsilon(\text{Sn}^{2+}, \text{Cl}^-) = (0.14 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$  (see Appendix A entry for [1928PRY]), Eq. (II.38)

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \xi$$

and accounting for  $a_{\text{Sn}}$  in a saturated tin amalgam [2003YEN/GRO],  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(26.72 \pm 0.71) \text{ kJ}\cdot\text{mol}^{-1}$  has been obtained.

Bond and Taylor [1970BON/TAY] report  $\Delta_r E^\circ$  (VI.12) =  $-0.374 \text{ V}$  for the reaction:



at  $25^\circ\text{C}$  and  $I = 1.0 \text{ M NaClO}_4$ .

For Reaction (VI.13):



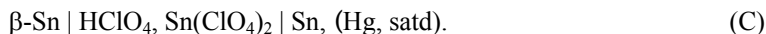
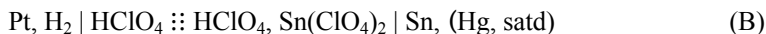
[1967KRA] obtained in the same ionic medium  $\Delta_r E^\circ$  (VI.13) =  $0.23227 \text{ V}$ . With  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) = (0.19 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$  and Eq. (II.38)  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(24.15 \pm 0.51) \text{ kJ}\cdot\text{mol}^{-1}$  has been obtained.

El Wakkad *et al.* [1957WAK/SAL] determined the standard potential of Reaction (VI.10) using a cell of the type:



where  $y \ll x$ , thus the liquid junction potential was considered negligible. The measurements were carried out under strictly air-free conditions and, for comparison, without this extreme protection as well. Unfortunately the originally measured  $E$  values are not given, so it was attempted to retrieve them from the  $E^\circ$  values given, see Appendix A. A SIT analysis with these  $E$  values resulted in  $E^\circ = -(0.1394 \pm 0.0005) \text{ V}$ , see Figure A-19. In view of the assumptions necessary to reproduce the original experimental data set the uncertainty was increased, so that the value accepted for statistical analysis,  $E^\circ = -(0.1394 \pm 0.0015) \text{ V}$  corresponding to  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(26.90 \pm 0.29) \text{ kJ}\cdot\text{mol}^{-1}$ , overlaps with the one given by the authors ( $E^\circ = -(0.1375 \pm 0.0005) \text{ V}$ ).

Vasil'ev and Glavina [1973VAS/GLA] determined the standard potential for Reaction (VI.10) in aqueous perchloric acid solutions using cells (B) and (C)



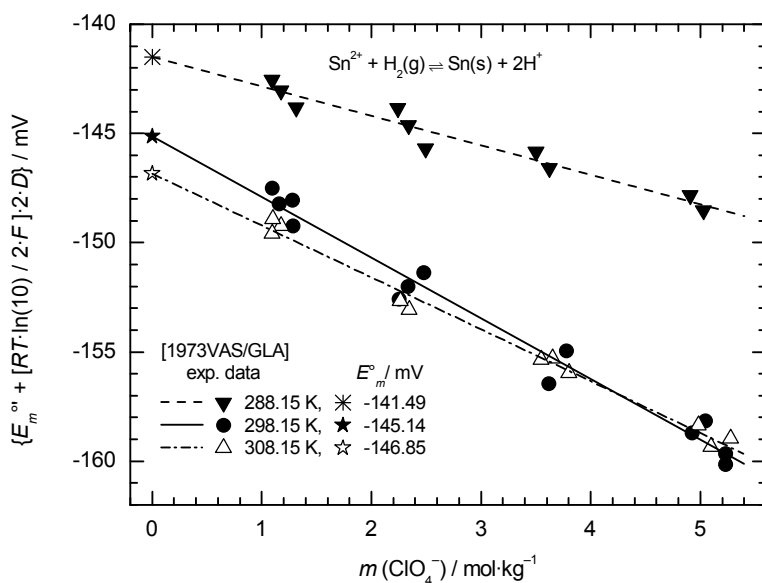
The potentials of these cells were measured at  $15, 25$  and  $35^\circ\text{C}$  in a concentration range of  $1.0, 2.0, 3.0, 4.0 \text{ M HClO}_4$  and  $0.017$  to  $0.11 \text{ M Sn}(\text{ClO}_4)_2$ . These data have been re-evaluated with the SIT model. Details are depicted in Figures A-33 to A-36. The results are summarised in Figure VI-1. A value for  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(28.01 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$  was obtained. The originally reported and recalculated values of  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  are listed in Table VI-1.



Table VI-1: Gibbs energy of formation of Sn<sup>2+</sup>.

Reference	$\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$		Method
	reported	recalculated	
[1917NOY/TOA]	$-28.17 \pm 0.39$	$-26.99 \pm 0.30$	$K^\circ$ (VI.6) measured, $E^\circ$ (VI.7) = $-0.132 \text{ V}$
[1928PRY]	$-26.17 \pm 0.12$	$-25.80 \pm 0.29$	$E^\circ$ : Sn   Sn <sup>2+</sup> :: 3.5 M calomel.
[1938HAR/WHI]	$-27.13 \pm 0.04$	$-27.20 \pm 0.12$	$E^\circ$ : Pt   H <sub>2</sub> (g)   HCl(x m) :: HCl(x m), SnCl <sub>2</sub> (y m)   Sn, x=100 y.
[1949RIC/POP]		$-26.72 \pm 0.71$	half-wave potential of Sn <sup>2+</sup> vs. normal calomel electrode
[1957WAK/SAL]	$-26.52 \pm 0.10$	$-26.88 \pm 0.29$	$E^\circ$ : Pt   H <sub>2</sub> (g)   HClO <sub>4</sub> (x m)   HClO <sub>4</sub> (x m), Sn(ClO <sub>4</sub> ) <sub>2</sub> (y m)   Sn, x >> y.
[1970BON/TAY]		$-24.15 \pm 0.51$	$E^\circ$ : Ag   AgCl   Cl <sup>-</sup> :: Sn <sup>2+</sup>   Sn (Hg)
[1973VAS/GLA]	$-27.87 \pm 0.08$	$-28.01 \pm 0.12$	$E^\circ$ : Pt, H <sub>2</sub>   H <sup>+</sup> :: H <sup>+</sup> , Sn <sup>2+</sup>   Sn <sub>s</sub> (Hg) <sub>sat</sub>

Figure VI-1: Re-evaluation of the results of [1973VAS/GLA] for reaction  $\text{Sn}^{2+} + \text{H}_2(\text{g}) \rightleftharpoons \beta\text{-Sn} + 2 \text{H}^+$  using the SIT. (▼: experimental data at 15 °C; dashed line: linear fit of the data at 15 °C; ●: experimental data at 25 °C; solid line: linear fit of the data at 25 °C; △: experimental data at 35 °C; dash dot line: linear fit of the data at 35 °C).



Although the values of [1949RIC/POP] and [1970BON/TAY] are not unreasonable they were not used for statistical analysis, because the experimental bases of the results of [1917NOY/TOA], [1928PRY], [1938HAR/WHI], [1957WAK/SAL] and [1973VAS/GLA] are far more convincing. Thus, the recalculated values of [1917NOY/TOA], [1928PRY], [1938HAR/WHI], [1957WAK/SAL] and [1973VAS/GLA] were weighted by their uncertainties resulting in a mean value of  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.39 \pm 0.08) \text{ kJ}\cdot\text{mol}^{-1}$ . It is recommended to increase the unrealistically low uncertainty so that the value selected in this review:

$$\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.39 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$$

overlaps with the CODATA key value,  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.60 \pm 0.40) \text{ kJ}\cdot\text{mol}^{-1}$  [1989COX/WAG].

## VI.2.2 Enthalpy of formation of $\text{Sn}^{2+}$

The standard enthalpy of formation of  $\text{Sn}^{2+}$  ion can be determined from the temperature dependence of the standard potentials of the  $\text{Sn}/\text{Sn}^{2+}$  electrode measured by Vasil'ev and Glavina [1973VAS/GLA]. The values listed in Table VI-2 refer to Reaction (VI.10), which is the reverse of the formation reaction (VI.8). A linear fit of recalculated values  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0))/T$  vs.  $1/T$ , weighted by uncertainties,

$$\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})/2F = \left( \frac{\partial (E^\circ(\text{Sn}^{2+}/\text{Sn})/T)}{\partial (1/T)} \right)_p$$

results in the standard enthalpy of  $\text{Sn}^{2+}$  formation to be:

$$\begin{aligned} \Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})/2F &= -(65.1 \pm 16.9) \text{ mV (recalculated);} \\ &\quad - (65.2 \pm 6.3) \text{ mV (original data)} \end{aligned}$$

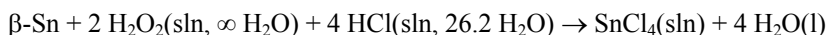
$$\begin{aligned} \Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) &= -(12.6 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1} \text{ (recalculated);} \\ &\quad - (12.6 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1} \text{ (reported).} \end{aligned}$$

Table VI-2: Standard potential of the reaction  $\text{Sn}^{2+} + \text{H}_2(\text{g}) \rightleftharpoons \beta\text{-Sn} + 2 \text{H}^+$  from [1973VAS/GLA].

$t / ^\circ\text{C}$	$E^\circ(\text{VI.8})/\text{mV}$ reported	$E^\circ(\text{VI.8})/\text{mV}$ recalculated	$K/T$	$E^\circ(\text{VI.8}) T^{-1}/\text{mV}\cdot\text{K}^{-1}$ recalculated	$E^\circ(\text{VI.8}) T^{-1}/\text{mV}\cdot\text{K}^{-1}$ reported
15	$-141.5 \pm 0.3$	$-141.49 \pm 0.82$	0.003470	$-0.4910 \pm 0.0028$	$-0.4911 \pm 0.0010$
25	$-144.5 \pm 0.4$	$-145.14 \pm 0.60$	0.003354	$-0.4868 \pm 0.0020$	$-0.4847 \pm 0.0013$
35	$-146.8 \pm 0.3$	$-146.85 \pm 0.78$	0.003245	$-0.4766 \pm 0.0025$	$-0.4764 \pm 0.0010$

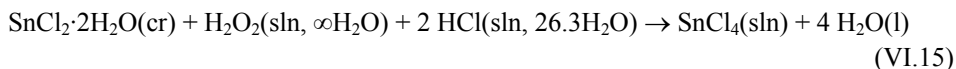
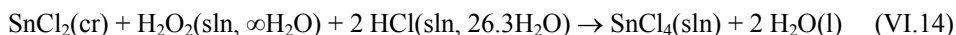
As only three data pairs ( $E^\circ$ ,  $T$ ) over a temperature range of 20 K are available the standard enthalpy of formation, thus obtained, seems rather doubtful.

Vasil'ev and coworkers attempted to determine  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  calorimetrically. In a first step the enthalpy of the following reaction



was investigated by [1973VAS/KOK] using a calorimeter, with an isothermal jacket, and with automatic recording of the temperature/time curves [1966VAS/LOB]. The reaction vessel, stirrer-ampoule holder, and casing of the calibrating heater were made of tantalum. It was demonstrated that this precision calorimeter works fine [1966VAS/LOB2]. So this calorimeter was used in the following steps too.

The heats of dissolution of  $\text{SnCl}_2(\text{cr})$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  in HCl solutions containing  $\text{H}_2\text{O}_2$  have been measured at 25 °C according to Reactions (VI.14) and (VI.15) [1973VAS/VAS2],

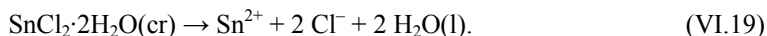


the standard enthalpies of formation of  $\text{SnCl}_2(\text{cr})$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  have been calculated using the results of [1973VAS/KOK].

Finally the standard enthalpy of formation of tin(II) chloride in perchloric acid solutions has been investigated calorimetrically [1973VAS/VAS], [1976VAS/KOK]. The dissolution of  $\text{SnCl}_2(\text{cr})$  in  $\text{HClO}_4$  solutions can be represented by the following reactions:



As the equations for dissolution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  are analogous, only Eq. (VI.19) needs to be given:



Equations (VI.16) to (VI.18) contribute to the measured value of  $\Delta_{\text{sln}} H$  of  $\text{SnCl}_2(\text{cr})$  according to Eq. (VI.20):

$$\Delta_{\text{sln}} H (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = \alpha_1 \Delta_r H (\text{VI.16}) + \alpha_2 \Delta_r H (\text{VI.17}) + \alpha_3 \Delta_r H (\text{VI.18}) \quad (\text{VI.20})$$

where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  in Eq. (VI.20) are the fractions of  $\text{Sn}^{2+}$ ,  $\text{SnCl}^+$  and  $\text{SnCl}_2$ ;  $\Delta_r H$  (VI.16),  $\Delta_r H$  (VI.17) and  $\Delta_r H$  (VI.18) are the enthalpy contributions of Reactions (VI.16) to (VI.18). For the calculation of  $\alpha_n$  the authors used the stability constants

given in Table A-33 Obviously only  $\Delta_r H$  (VI.16) and  $\Delta_r H$  (VI.17) could be evaluated with sufficient accuracy to justify extrapolation to infinite dilution.

Recalculation with a set of constants, selected by this review, is in principle possible only when the composition of the solutions used for calorimetry can be ascertained. This is the case for the experimental data at 25 °C listed in [1973VAS/VAS], but not for those at 10 °C presented graphically in [1976VAS/KOK]. For the evaluation of  $\Delta_f H_m^\circ$  ( $\text{Sn}^{2+}$ , 298.15 K) only Reaction (VI.16) and (VI.19) are relevant. Consequently extrapolation of  $\Delta_r H$  (VI.16) for  $\text{SnCl}_2(\text{cr})$  and  $\Delta_r H$  (VI.19) for  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  to  $I \rightarrow 0$  was based on 1) the data listed in Table VI-3 for 25 °C taken from [1976VAS/KOK] and 2) the values of  $\Delta_r H$  (VI.16) and  $\Delta_r H$  (VI.19) recalculated in this review and listed in Table VI-4.

Table VI-3: Enthalpies of Reactions (VI.16) and (VI.19) at 25 °C from [1976VAS/KOK].

$I_c/\text{mol} \cdot \text{dm}^{-3}$ ( $\text{HClO}_4$ )	$I_m/\text{mol} \cdot \text{kg}^{-1}$ ( $\text{HClO}_4$ )	$\text{SnCl}_2(\text{cr})$ $\Delta_r H$ (VI.16)/ $\text{kJ} \cdot \text{mol}^{-1}$	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ $\Delta_r H$ (VI.19)/ $\text{kJ} \cdot \text{mol}^{-1}$
0.5	0.5133	$-10.251 \pm 1.004$	$7.573 \pm 0.209$
1.0	1.0508	$-9.163 \pm 0.335$	$8.745 \pm 0.335$
2.0	2.2038	$-6.402 \pm 0.377$	$11.966 \pm 0.167$
3.0	3.4713	$-3.012 \pm 0.418$	$15.188 \pm 0.209$

Table VI-4: Enthalpies of Reactions (VI.16) and (VI.19) at 25 °C from [1973VAS/VAS].

$I_c/\text{mol} \cdot \text{dm}^{-3}$ ( $\text{HClO}_4$ )	$I_m/\text{mol} \cdot \text{kg}^{-1}$ ( $\text{HClO}_4$ )	$\text{SnCl}_2(\text{cr})$ $\Delta_r H$ (VI.16)/ $\text{kJ} \cdot \text{mol}^{-1}$	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ $\Delta_r H$ (VI.19)/ $\text{kJ} \cdot \text{mol}^{-1}$
0.20	0.2025	$-13.0 \pm 0.2$	$5.3 \pm 0.7$
0.49	0.5027		$7.4 \pm 0.2$
1.02	1.0722	$-9.4 \pm 0.3$	$8.7 \pm 0.5$
1.96	2.1545	$-6.6 \pm 0.4$	$11.6 \pm 0.4$
2.93	3.3790	$-3.0 \pm 0.5$	$14.6 \pm 0.6$

The SIT approach to extrapolate enthalpies of reaction in electrolyte systems to infinite dilution is described in [1997ALL/BAN] and [1996PLY/GRE], who criticised the methods proposed by [1967VAS] and [1978VAS/YAS2]. This evoked a controversy between Vasil'ev [1997VAS] and Plyasunov and Grenthe [1998PLY/GRE]. The present review agrees with the thermodynamic argument put forward by [1996PLY/GRE] and adopts the SIT approach. For a comparison between Vasil'ev's [1967VAS], Vasil'ev and Yasinskii's [1978VAS/YAS] and the SIT method, see

Figures A-37 to A-40. As predicted by [1996PLY/GRE] the difference between Vasil'ev and SIT values is not large but perceptible.

The calculation of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  from thermochemical data of [1973VAS/KOK], [1973VAS/VAS2], [1973VAS/VAS] and [1976VAS/KOK] as well as NEA-TDB auxiliary data is summarised in Table VI-5. For the re-evaluation of Vasil'ev *et al.*'s the uncertainty was set to  $4\sigma$  (see also Figures A-37 and A-40). Consequently the SIT value appears to be less precise than that obtained by the authors' method [1967VAS], [1978VAS/YAS]. With the values of the enthalpies of Reactions (VI.16) and (VI.19) recalculated in this review (see Table VI-4), the values of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  derived from  $\Delta_r H$  (VI.16) and  $\Delta_r H$  (VI.19) agree with each other perfectly, thus the corresponding mean value was selected.

Table VI-5: Calculation of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  from thermochemical data.

	$[\Delta_{\text{diss}} H_m^\circ(\text{SnCl}_2)]$	$+ \Delta_f H_m^\circ(\text{SnCl}_2, \text{cr})$	$- 2\Delta_f H_m^\circ(\text{Cl}^-)$	$= \Delta_f H_m^\circ(\text{Sn}^{2+})/\text{kJ}\cdot\text{mol}^{-1}$	
[1976VAS/KOK]	$-(13.81 \pm 1.00)$	$-(327.86 \pm 1.09)$	$-(167.08 \pm 0.10) \times 2$	$-(7.51 \pm 1.49)$	
[1976VAS/KOK] recalc. using SIT	$-(15.05 \pm 0.93)$	$-(328.01 \pm 2.08)$	$-(167.08 \pm 0.10) \times 2$	$-(8.90 \pm 2.29)$	
[1973VAS/VAS], [1973VAS/VAS2], [1976VAS/KOK], recalc. this review	$-(15.83 \pm 0.20)$	$-(327.9 \pm 2.2)$	$-(167.08 \pm 0.10) \times 2$	$-(9.57 \pm 2.22)$	
	$[\Delta_{\text{diss}} H_m^\circ(\text{SnCl}_2) + \Delta_f H_m^\circ(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}) - 2\Delta_f H_m^\circ(\text{Cl}^-) - 2\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = \Delta_f H_m^\circ(\text{Sn}^{2+})]/\text{kJ}\cdot\text{mol}^{-1}$				
[1976VAS/KOK]	$(4.40 \pm 0.45)$	$-(918.26 \pm 1.42)$	$-(167.08 \pm 0.10) \times 2$	$-(285.83 \pm 0.04) \times 2$	$-(8.04 \pm 1.50)$
[1976VAS/KOK] recalc. using SIT	$(3.19 \pm 0.43)$	$-(918.95 \pm 2.74)$	$-(167.08 \pm 0.10) \times 2$	$-(285.83 \pm 0.04) \times 2$	$-(9.94 \pm 2.78)$
[1973VAS/VAS], [1973VAS/VAS2], [1976VAS/KOK], recalc. this review	$(3.01 \pm 0.14)$	$-(918.26 \pm 2.75)$	$-(167.08 \pm 0.10) \times 2$	$-(285.83 \pm 0.04) \times 2$	$-(9.43 \pm 2.76)$
[1976VAS/KOK] recal. SIT $\rightarrow \Delta_f H_m^\circ(\text{Sn}^{2+})/\text{kJ}\cdot\text{mol}^{-1}$			this review, all data $\rightarrow \Delta_f H_m^\circ(\text{Sn}^{2+})/\text{kJ}\cdot\text{mol}^{-1}$		
Eq. (VI.16)		$-(8.90 \pm 2.29)$	Eq. (VI.16)	$-(9.57 \pm 2.22)$	
Eq. (VI.19)		$-(9.94 \pm 2.78)$	Eq. (VI.19)	$-(9.43 \pm 2.76)$	
weighted mean		$-(9.32 \pm 1.77)$	weighted mean	$-(9.52 \pm 1.73)$	

Vasil'ev and Glavina [1973VAS/GLA]:  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(12.6 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$

SIT [1976VAS/KOK]:  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(9.3 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$

Vasil'ev *et al.*'s data [1973VAS/VAS], [1973VAS/VAS2], [1976VAS/KOK] recalculated by this review:  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(9.5 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ .

In any case the calorimetrically determined value of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  is far more reliable than the value derived above from the three data pairs  $E^\circ$ ,  $T$  of Reaction (VI.10). Consequently, the weighted mean of the two calorimetrically determined values was selected in this review

$$\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(9.42 \pm 1.24) \text{ kJ}\cdot\text{mol}^{-1}$$

and overlaps with the CODATA key value,  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(8.9 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  [1989COX/WAG].

### VI.2.3 Partial molar entropy of $\text{Sn}^{2+}$

When the selected values for  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.39 \pm 0.30) \text{ k}\cdot\text{mol}^{-1}$  (see Section VI.2.1) and  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(9.42 \pm 1.24) \text{ k}\cdot\text{mol}^{-1}$  (see Section VI.2.2) are employed,  $\Delta_f S_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  can be calculated by Eq. (VI.21) where  $T_{\text{ref}} = 298.15 \text{ K}$ :

$$\Delta_f S_m^\circ(\text{Sn}^{2+}) = \frac{\Delta_f H_m^\circ(\text{Sn}^{2+}) - \Delta_f G_m^\circ(\text{Sn}^{2+})}{T_{\text{ref}}}. \quad (\text{VI.21})$$

The partial molar entropy of  $\text{Sn}^{2+}$  follows from Eq. (VI.22):

$$S_m^\circ(\text{Sn}^{2+}) = \Delta_f S_m^\circ(\text{Sn}^{2+}) - S_m^\circ(\text{H}_2, \text{g}) + S_m^\circ(\text{Sn, white}). \quad (\text{VI.22})$$

Taking  $S_m^\circ(\text{H}_2, \text{g})$  from the NEA TDB auxiliary data and  $S_m^\circ(\text{Sn, cr, white})$  as selected by this review, results in:

$$S_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(19.2 \pm 4.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This overlaps with the CODATA key value  $S_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(16.7 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [1989COX/WAG].

## VI.3 $\text{Sn}^{4+}$

There seems to be only one paper [1934PRY] in which it was attempted to determine the Gibbs energy of formation of  $\text{Sn}^{4+}$  ion,  $\Delta_f G_m^\circ(\text{Sn}^{4+})$ , directly by investigating Reaction (VI.23).



Potentiometric measurements were carried out in aqueous perchlorate medium using the cell  $\text{Sn} | \text{Sn}(\text{ClO}_4)_4, \text{HClO}_4 : 3.5 \text{ M KCl} : 3.5 \text{ M KCl} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ .

The result did not qualify for selection within this review, see Appendix A. Another possibility to obtain this base quantity is to combine Reaction (VI.10),  $\text{Sn}^{2+} + \text{H}_2(\text{g}) \rightleftharpoons \text{Sn}(\text{white}) + 2 \text{H}^+$  with



$$\Delta_f G_m^\circ(\text{Sn}^{4+}) = -\Delta_f G_m^\circ(\text{VI.24}) - \Delta_f G_m^\circ(\text{Sn}^{2+}).$$

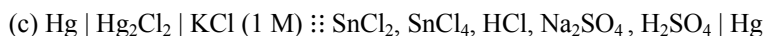
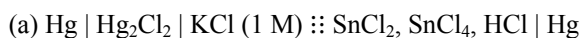
A value of  $\Delta_f G_m^\circ(\text{Sn}^{2+})$  has been selected in this review, and the critical assessment of all the investigations of Reaction (VI.24) is reported in Section VI.3.1.

### VI.3.1 Redox reaction $\text{Sn}^{4+}/\text{Sn}^{2+}$

The redox couple  $\text{Sn}^{4+}/\text{Sn}^{2+}$  according to Reaction (VI.24) is thermodynamically the connecting link between aqueous tin(IV) and tin(II) chemistry [2001SEB/POT]. Surprisingly limited reliable thermodynamic data are available in the literature for aqueous chemistry of tin(IV) [2002HUM/BER]. Until recently values of the standard electrode potential  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  were reported in four papers only, see Table VI-6, and all suffer from major deficiencies as discussed in the respective Appendix A entries.

Table VI-6:  $E^\circ$  of  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple at 298.15 K.

$E^\circ$ /mV	medium	method	deficiencies	authors
recalc.			$\text{Sn}(\text{IV})$ , $\text{Sn}(\text{II})$ chlorido and hydroxido complexes?	
$144 \pm 2$	1.0 - 5.3 M HCl	cell (a)		[1914FOR/BAR]
original			$\text{Sn}(\text{IV})$ , $\text{Sn}(\text{II})$ chlorido and hydroxido complexes?	
$154 \pm 3$	0.10 - 2.02 M HCl	cell (b)		[1934HUE/TAR]
original	4 M HCl,		$\text{Sn}(\text{IV})$ chlorido, sulphato complexes?	
$228 \pm ?$	1 M $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{SO}_4$	cell (c)	Extrapolation $I \rightarrow 0$ ?	[1972DES/JOV]
original			$\text{Sn}(\text{IV})$ chlorido complexes neglected!	
$152.2 \pm 0.5$	2 - 4 M $\text{HClO}_4$	cell (d)	sign error!	[1979VAS/GLA]



Clearly the mixed chloride and sulfate medium of Despić *et al.* [1972DES/JOV] obscures the extrapolation to zero ionic strength. Thus the value of Vasil'ev *et al.* [1979VAS/GLA] seemed to confirm the generally accepted result of Huey and Tartar [1934HUE/TAR]. As the value of Forbes and Bartlett [1914FOR/BAR] deviates less than 10 mV from the mean value of the former ones, Latimer's [1952LAT] selection  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (150 \pm 10)$  mV seemed amply justified [1974POU], [1982WAG/EVA]. Re-evaluation of the data listed in [1979VAS/GLA], however, shows that the results are flawed by two numerical mistakes.

- (1) While the equations used for extrapolation to ionic strength  $I = 0$  are quite correct and similar to those of the SIT approach,  $-\psi(I)$  has erroneously been ascribed a negative value. This sign error was detected by Hummel *et al.* [2002HUM/BER].



$$E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = E_c^\circ + \frac{RT \ln(10)}{2F} \left( \frac{\Delta z^2 A \sqrt{I}}{1 + 1.6\sqrt{I}} + bI \right) \quad \text{Eq. (6), [1979VAS/GLA]}$$

$$\Delta z^2 = -10$$

$$\psi(I) = \frac{RT \ln(10)}{2F} \left( \frac{\Delta z^2 A \sqrt{I}}{1 + 1.6\sqrt{I}} \right) \quad \text{Eq. (7), [1979VAS/GLA]}$$

$$E_c^{\circ'} - \psi(I) = E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) + \frac{RT \ln(10)}{2F} bI \quad \text{Eq. (8), [1979VAS/GLA]}$$

- (2) Table 2 of [1979VAS/GLA] contains the experimental values, but some data must be exchanged, see Appendix A for details.

In order to carry out a SIT analysis based on molality as composition variable the corrected data were transformed accordingly, see the Appendix A entry for [1979VAS/GLA]. Correctly calculated Vasil'ev *et al.*'s data result in a standard electrode potential of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}, 298.15 \text{ K}) = (274.0 \pm 10) \text{ mV}$ , which differs by more than 120 mV from the value generally accepted.

Now the question arises how Vasil'ev *et al.* dealt with Sn(II) and Sn(IV) hydroxido and chlorido complexes in order to find out the concentrations of free  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  ions. Sn(II) hydroxido complexes have to be considered in 2 to 4 M  $\text{HClO}_4$  solutions, but only the single experimental study of Nazarenko *et al.* [1971NAZ/ANT] is available on the hydrolysis of tin(IV) under acidic conditions. Because several experimental details are debatable the results of this investigation can be regarded as approximate estimates only. Using different correlations with  $\text{Zr}^{4+}$  the presence of 10 to 50% hydrolyzed species may be predicted in 4.5 M  $\text{HClO}_4$  solution [2009GAJ/SIP]. On the other hand, the UV spectra of main group metal ions show considerable changes during hydrolysis [1997SIP/CAP], [2001PER/HEF]. The UV spectra of tin(IV) in 3 to 8 M  $\text{HClO}_4$  are nearly identical, indicating only small (if any) changes in the speciation [2009GAJ/SIP]. This observation renders the above mentioned correlations unreliable and supports an approach, which neglects the formation of hydroxido species at  $c_{\text{HClO}_4} \geq 4.5 \text{ M}$ .

In addition Vasil'ev *et al.* [1979VAS/GLA] assume that no Sn(IV) chlorido complexes form in the pertinent medium. This has been concluded from experiments of Vasil'ev and Glavina [1976VAS/GLA] and [1977VAS/GLA] where  $\text{SnCl}_4$  and



$(\text{NH}_4)_2\text{SnCl}_6$  seemed to dissociate completely in 0.6 – 2.0 M  $\text{HClO}_4$ . The conclusion drawn from these surprising observations clearly contradicts the results of Fatouros *et al.* [1978FAT/ROU] who based their study of Sn(IV) chlorido complexes on a symmetric cell without liquid junction, see the Appendix A entry for [1978FAT/ROU]. Fatouros *et al.* found the complete series from  $\text{SnCl}_3^+$  to  $\text{SnCl}_6^{2-}$  in 5 M  $\text{HClO}_4$  solutions, where Sn(IV) hydroxido complex formation should essentially be suppressed. The stability constants of the Sn(IV) chlorido complexes range from  $3 < \log_{10} \beta^{\circ} < 11$ .

A rationale of these seemingly contradictory experimental results could be that hydrolysis, which certainly is effective in 0.6 to 2 M  $\text{HClO}_4$  [1977VAS/GLA], and dissociation cannot be distinguished by measurements with Vasil'ev and Glavina's cells.

Thus, the assumed link [2001SEB/POT] between aqueous tin(IV) and tin(II) chemistry has been in fact missing! This prompted Gajda *et al.* [2009GAJ/SIP] to perform potentiometric studies to determine  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+})$  in strongly acidic solution, in order to suppress as far as possible hydrolytic processes leading to Sn(IV) hydroxido complexes of unknown stability. However, due to several experimental difficulties (see Appendix A) only the experiments performed in  $(I - 1)$  M  $\text{HClO}_4 + 1$  M  $\text{HCl}$ ,  $(I - 1) = 3, 4, 5$  M) provided reliable  $\text{Sn}^{4+}/\text{Sn}^{2+}$  redox potentials, which necessitated the determination of the stepwise formation constants of  $\text{SnCl}_x^{4-x}$  complexes in 4.5 to 8.0 M  $\text{HClO}_4$  solutions, too (see Section VIII.3.2.2).

For the electrochemical measurements involving chloride containing mixed background electrolyte the electrochemical cell (Z) (with  $(I - 1) = 3, 4, 5$  M) was employed.

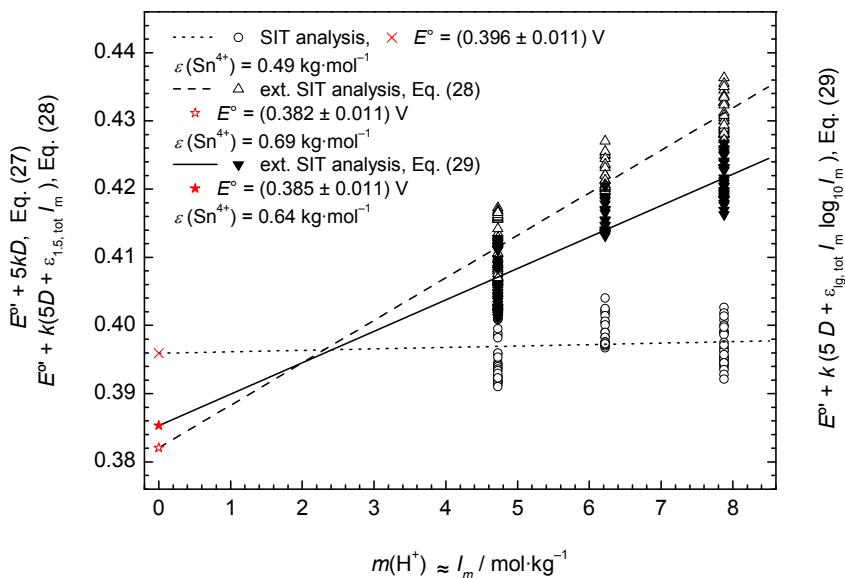
$\text{Pt, H}_2 | 1 \text{ M HCl}, (I - 1) \text{ M HClO}_4 :: x \text{ M SnCl}_2, y \text{ M SnCl}_4, 1 \text{ M HCl}, (I - 1) \text{ M HClO}_4 | \text{Hg}$  (Z)

Under such conditions, the electrode potentials were found to be stable within  $\pm 0.2$  mV after 30 – 60 minutes (as the system is relatively “well buffered” against  $\text{O}_2$ -traces). The reproducibility of the parallel runs were found to be reasonable ( $\pm 4$  mV, see the Appendix A entry for [2009GAJ/SIP]), the slope of the experimental plots was found to be close to the theoretical value (29.58 mV/decade). The evaluation of the experimental data required the knowledge of the formation constants  $\beta_x$  of tin(II) and tin(IV) chlorido complexes at a given ionic strength  $I$ . Since a mixed background electrolyte has been used, the true formation constants are not available. In the case of tin(IV) the constants determined for  $\text{HClO}_4$  background were used to extra/interpolate to the given ionic strength. In the case of tin(II) the data set for  $\text{NaClO}_4$  background electrolyte, selected in this review, has been used. Although, in the case of tin(II),  $\beta_1$  and  $\beta_2$  determined for  $\text{NaClO}_4$  could be converted to  $\text{HClO}_4$ , similar conversions cannot be made for  $\beta_3$  ( $\varepsilon(\text{H}^+, \text{SnCl}_3^-)$  is unknown) and  $\beta_4$  ( $\Delta\varepsilon$  and  $\varepsilon(\text{H}^+, \text{SnCl}_4^{2-})$  are unknown). In addition, a mixed background electrolyte was used, therefore it seemed more reliable to assume similar ionic strength dependence in  $\text{NaClO}_4$  and  $\text{HClO}_4/\text{HCl}$  background electrolytes.

The experimentally observed potential values as a function of  $\log_{10}([\text{Sn}^{4+}_{\text{free}}]/[\text{Sn}^{2+}_{\text{free}}])$  are depicted in the Appendix A entry for [2009GAJ/SIP]. The extrapolation to  $\log_{10}([\text{Sn}^{4+}_{\text{free}}]/[\text{Sn}^{2+}_{\text{free}}]) = 0$  resulted in the formal potentials  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+})$  at the different ionic strengths applied. Considering the uncertainties related to the formation constants of the chlorido complexes and the mixed background electrolyte, the uncertainties of  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+})$  have been assigned three times the mean deviation between the measured and calculated  $E$  values of cell (Z).

The extrapolation of the determined standard potentials to zero ionic strength by linear regression and error propagation assuming Gaussian probability distribution applying the SIT approach (Figure VI-2, dotted line) resulted in  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.396 \pm 0.011)$  V. However, at  $I_m > 3 \text{ mol}\cdot\text{kg}^{-1}$  HClO<sub>4</sub> solution the activity coefficients deviate strongly from those calculated by the simple SIT approach. Therefore, the use of extended SIT is more appropriate in this case. There are two accepted ways to extend the validity of SIT to high ionic strengths. Simple and extended SIT approaches on the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  redox Reaction (VI.24) are summarised in Eqs. (VI.25) to (VI.29), where  $k = RT \ln(10)/F$ , and  $D$  is the Debye-Hückel term.

Figure VI-2: Extrapolation of the  $E^{\circ}$  data of cell (Z) for reaction  $\text{Sn}^{4+} + \text{H}_2(\text{g}) \rightleftharpoons \text{Sn}^{2+} + 2 \text{H}^+$  to  $I = 0$  using the SIT (dotted line, calculated by Eq. (VI.27)) and extended SIT (dashed line – Eq. (VI.28) and solid line – Eq. (VI.29)).





$$E^\circ = E - \frac{k}{2} \left\{ \log_{10} \left[ \frac{m_{\text{Sn}^{4+}} P_{\text{H}_2}}{m_{\text{Sn}^{2+}} m_{\text{H}^+}^2} \right] + \log_{10} \left[ \frac{\gamma_{\text{Sn}^{4+}}}{\gamma_{\text{Sn}^{2+}} \gamma_{\text{H}^+}^2} \right] \right\} \quad (\text{VI.25})$$

$$E^{\circ 1} = E - \frac{k}{2} \log_{10} \left[ \frac{m_{\text{Sn}^{4+}} P_{\text{H}_2}}{m_{\text{Sn}^{2+}} m_{\text{H}^+}^2} \right] \quad (\text{VI.26})$$

$$E^{\circ 1} + (k/2) \cdot 10D = E^\circ + (k/2) \cdot \Delta\varepsilon \cdot I_m \quad (\text{VI.27})$$

$$E^{\circ 1} + (k/2) [10D + 2\varepsilon_{1.5} \cdot I_m^{1.5}] = E^\circ + (k/2) \Delta\varepsilon \cdot I_m \quad (\text{VI.28})$$

$$E^{\circ 1} + (k/2) \cdot (10D + 2\varepsilon_{\text{lg}} I_m \cdot \log_{10} I_m) = E^\circ + (k/2) \cdot \Delta\varepsilon I_m \quad (\text{VI.29})$$

The estimation of numerical values for  $\varepsilon_{1.5}$  and  $\varepsilon_{\text{lg}}$  is described in the Appendix A entry for [2009GAJ/SIP]. From Eqs. (VI.28) and (VI.29) (Figure VI-2, dashed and solid line)  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.382 \pm 0.011)$  V and  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.385 \pm 0.011)$  V can be calculated. From the slopes of the dashed and solid line in Figure VI-2  $\Delta\varepsilon = 0.21$  and  $0.16 \text{ kg}\cdot\text{mol}^{-1}$  can be derived for Reaction (VI.24), which corresponds to  $\varepsilon(\text{Sn}^{4+}, \text{ClO}_4^-) = 0.69$  and  $0.64 \text{ kg}\cdot\text{mol}^{-1}$ , respectively. Although, these values are somewhat smaller than expected for an  $\text{M}^{4+}$  cation, they are obviously much higher than  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) = 0.19 \text{ kg}\cdot\text{mol}^{-1}$  selected in this review.

The above  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  value is more positive than the so far generally accepted value of 0.15 V. The latter value was based on measurements conducted in HCl media, however the formation of chlorido complexes was neglected. Since tin(IV) forms much more stable chlorido complexes than tin(II), and therefore  $[\text{Sn}^{4+}_{\text{free}}]/[\text{Sn}^{2+}_{\text{free}}] \ll [\text{Sn(IV)}]_{\text{tot}}/[\text{Sn(II)}]_{\text{tot}}$ , the considerably more positive value determined by [2009GAJ/SIP] is understandable. Indeed, assuming identical ionic strength dependence of tin(II)- and tin(IV)-chlorido complexes in perchlorate and chloride media,  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) \approx 0.36$  V can be estimated from Huey and Tartar's data [1934HUE/TAR], which validates the high positive value.

The relatively high uncertainty of  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  originates from the uncertainties associated with both formation constants and the applied mixed background electrolyte. The extrapolation to  $I_m = 0$  poses the same problem as mentioned above for the formation constants of chlorido complexes, therefore a standard potential  $E^{\circ 1}(\text{Sn}^{4+}/\text{Sn}^{2+}, 6.41 \text{ m (5 M) HClO}_4) = (0.318 \pm 0.011)$  V has been defined. For the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  standard electrode potential a larger uncertainty has been estimated, because of the long extrapolation to  $I_m = 0$  which has to be taken into account, thus

$$E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}, 298.15 \text{ K}) = (0.384 \pm 0.020) \text{ V}$$

has been selected in this review. Due to the experimental limitations, high ionic strength and mixed background electrolyte, the ion interaction coefficient can be estimated only crudely  $\varepsilon(\text{Sn}^{4+}, \text{ClO}_4^-, 298.15 \text{ K}) = (0.7 \pm 0.2) \text{ kg mol}^{-1}$ .

As indicated in the beginning of Section VI.3 selected values for  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  and  $\Delta_r G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  enable selection of

$$\Delta_r G_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) = (46.7 \pm 3.9) \text{ kJ mol}^{-1}.$$

### VI.3.2 Entropy estimation methods for aqueous tin(IV) ion

As discussed in Chapter X of [1997ALL/BAN] there are several methods available to estimate entropies of aqueous species. These methods use correlations between ionic entropies and a combination of crystallographic radii, molar mass, molar volume, electrical charge etc. The most reliable effective ionic radii for metal ions are listed in [1976SHA]. Unfortunately no ionic radius can be defined for  $\text{Sn}^{2+}$ , see Appendix A entry on [1976SHA].

With  $\text{Sn}^{4+}$  the situation is quite different, as pointed out in Appendix A entry on [1951POW/LAT]. A modified Powell-Latimer correlation was based on 33 experimentally determined and comparatively reliable entropies of monatomic uni-, di-, tri-, and tetravalent cations, see Figure VI-3.

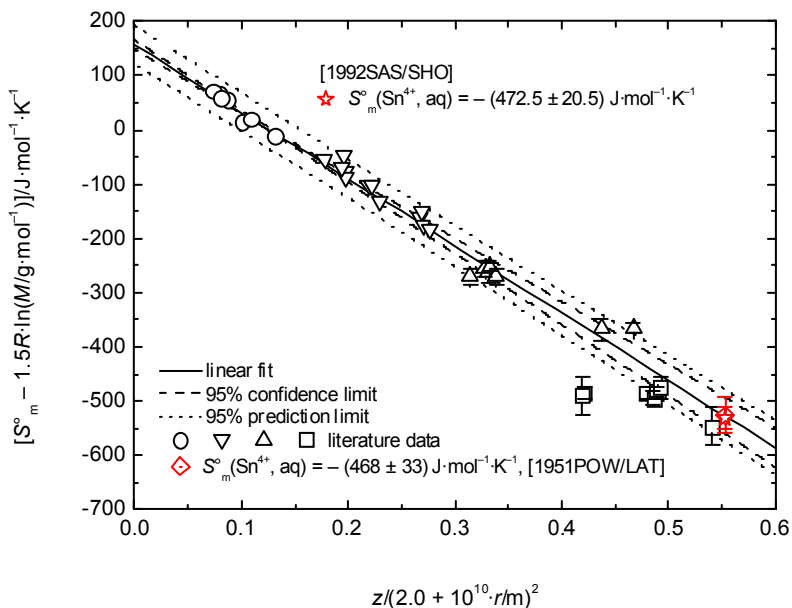
This modified Powell-Latimer correlation led to  $S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) = -(468 \pm 33) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

When the correlation functions suggested by [1992SAS/SHO] are applied (see Appendix A) to the 33 monatomic cations, the average absolute difference ( $\delta S_m^\circ$ ) between the measured and calculated  $S_m^\circ$  values,  $\delta S_m^\circ = 10.23 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . By this method, the partial molar entropy of  $\text{Sn}^{4+}$  can be estimated to be:

$$S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) = -(472.5 \pm 20.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

where the uncertainty has been taken twice the average value of the 33 monatomic cations mentioned above. Although the correlation functions of [1992SAS/SHO] and [1951POW/LAT] are different, the predicted values of  $S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K})$  as well as the estimated uncertainties are similar. While only experimentally determined values can be selected,  $S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) = -(472.5 \pm 20.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is the best estimate for this quantity obtained by this review.

Figure VI-3: Modified Powell-Latimer correlation between ionic entropies and a combination of crystallographic radii, molar mass, electrical charge. ○: univalent cations; ▽: divalent cations; ▽: trivalent cations; □: tetravalent cations; ◇:  $\text{Sn}^{4+}$ , calculated using the modified Powell-Latimer correlation; solid line: linear fit; dashed line: 95% confidence limits; dotted line: 95% prediction limits; ☆: least squares value of Powell-Latimer function for  $\text{Sn}^{4+}$  (298.15 K).





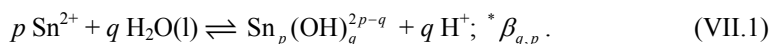
# Chapter VII

## Tin oxygen and hydrogen compounds and complexes

### VII.1 Aqueous tin hydroxido complexes

#### VII.1.1 Tin(II) hydroxido complexes

Tin(II) has a strong tendency to hydrolysis, and forms several aqueous hydroxido complexes depending on the pH and metal ion concentration. The hydrolytic reactions can be defined by the following generalised equilibrium process:



Relatively few reports are available on the equilibrium properties of tin(II) hydroxido complexes, which is probably related to the easy oxidation of tin(II) and to precipitation that occurs at a low degree of hydrolysis. The hydrolysis constants reported in the literature are collected in Table VII-1. There are some discrepancies among the authors concerning the composition of the complexes formed in the acidic region. The species  $\text{SnOH}^+$  was identified in all studies, except in [1991DJO/ZMB]. After the work of Tobias [1958TOB], the formation of  $\text{Sn}_3(\text{OH})_4^{2+}$  as the dominating hydrolytic species at  $[\text{Sn}^{2+}]_{\text{tot}} > 0.1 \text{ mM}$ , became widely accepted. In the earlier publications insufficient data are provided, therefore their re-evaluation considering the formation of the trinuclear complex is not possible. Pettine *et al.* [1981PET/MIL] used a very low concentration of tin(II), hence only mononuclear hydroxido complexes were detected. In [1958TOB] and [1991DJO/ZMB], the formation of the dinuclear  $\text{Sn}_2(\text{OH})_2^{2+}$  species was reported, too, however the results published in [1976GOB] and [1997SAL/FER] did not justify its presence. The re-evaluation of the data reported in [1958TOB] by the reviewers, confirmed the conclusion of [1976GOB] and [1997SAL/FER] (see Appendix A entry for [1958TOB]).

Consequently, before the formation of  $\text{Sn}(\text{OH})_2$  the following equilibria should be considered

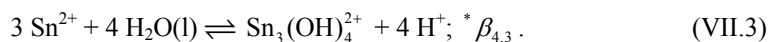
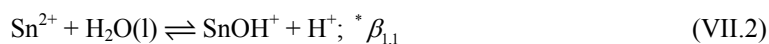


Table VII-1: Experimental equilibrium data for the hydrolysis of tin(II).

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_a$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SnOH}^+ + \text{H}^+$						
gl	$\rightarrow 0$ ((Na,H)ClO <sub>4</sub> )	25	-1.70			[1939GOR]
sol	$\rightarrow 0$ (HCl)	25	-2.07			[1941GAR/HEI]
pot	3 M NaClO <sub>4</sub>	25	-1.70 ± 0.08			[1952VAN/RHO]
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-3.92 ± 0.15	-3.75 ± 0.01	-3.68 ± 0.10	[1958TOB]
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-3.70 ± 0.02	-3.70 ± 0.01	-3.63 ± 0.10	[1976GOB]
vol	0.1 M NaNO <sub>3</sub>	20	-4.1 ± 0.2	-3.73 ± 0.40	-3.73 ± 0.40	[1981PET/MIL]
	0.5 M NaNO <sub>3</sub>		-3.8 ± 0.2	-3.85 ± 0.40	-3.84 ± 0.40	
	1.0 M NaNO <sub>3</sub>		-4.1 ± 0.2	-3.83 ± 0.40	-3.81 ± 0.40	
	0.5 M NaCl		-3.1 ± 0.2	-2.97 ± 0.40	-2.96 ± 0.40	
gl	3 M NaCl	25	-2.18 ± 0.02			[1995DJU/JEL]
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-3.77 ± 0.05		-3.70 ± 0.20	[1997SAL/FER]
$3 \text{Sn}^{2+} + 4 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}_3(\text{OH})_4^{2+} + 4 \text{H}^+$						
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-6.77 ± 0.03	-6.73 ± 0.01	-6.60 ± 0.10	[1958TOB]
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-6.81 ± 0.03	-6.81 ± 0.01	-6.68 ± 0.10	[1976GOB]
gl	0.5 M NaClO <sub>4</sub>	25	-6.30 ± 0.10		-6.30 ± 0.40	[1991DJO/ZMB]
gl	3 M NaCl	25	-2.70 ± 0.01			[1995DJU/JEL]
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-6.87 ± 0.09		-6.74 ± 0.20	[1997SAL/FER]
$2 \text{Sn}^{2+} + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}_2(\text{OH})_2^{2+} + 2 \text{H}^+$						
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-4.45 ± 0.15			[1958TOB]
gl	0.5 M NaClO <sub>4</sub>	25	-4.59 ± 0.08			[1991DJO/ZMB]
$\text{Sn}^{2+} + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_2(\text{aq}) + 2 \text{H}^+$						
sol	$\rightarrow 0$ (HCl)	25	-7.06			[1941GAR/HEI]
vol	0.1 M NaNO <sub>3</sub>	20	-7.9 ± 0.2	-7.89 ± 0.40	-7.88 ± 0.40	[1981PET/MIL]
	0.5 M NaNO <sub>3</sub>		-7.9 ± 0.2	-7.87 ± 0.40	-7.85 ± 0.40	
	1.0 M NaNO <sub>3</sub>		-7.8 ± 0.2	-7.83 ± 0.40	-7.80 ± 0.40	
	0.5 M NaCl		-8.2 ± 0.2	-8.22 ± 0.40	-8.20 ± 0.40	
$\text{Sn}^{2+} + 3 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_3^- + 3 \text{H}^+$						
sol	$\rightarrow 0$ (NaOH)	25	-16.61	-17.22 ± 0.40	-17.22 ± 0.40	[1941GAR/HEI]
Ise-Sn	3 M NaClO <sub>4</sub>	25	-18.02 ± 0.04		-17.82 ± 0.20	[1977MAR]
Ise-Sn	3 M NaClO <sub>4</sub>	25	-17.8		-17.6 ± 0.3	[1977SMI/KRA]
pot	$\rightarrow 0$ (NaOH)	25	-16.88		-16.88 ± 0.30	[1978DIC/LOT]
vol	0.1 M NaNO <sub>3</sub>	20	-17.5 ± 0.2	-17.56 ± 0.40	-17.55 ± 0.40	[1981PET/MIL]
	0.5 M NaNO <sub>3</sub>		-17.7 ± 0.2	-17.58 ± 0.40	-17.56 ± 0.40	
	1.0 M NaNO <sub>3</sub>		-17.6 ± 0.2	-17.57 ± 0.40	-17.52 ± 0.40	
	0.5 M NaCl		-17.8 ± 0.2	-17.99 ± 0.40	-17.97 ± 0.40	
Ise-Sn,gl	3 M NaClO <sub>4</sub>	25	-15.9 ± 0.1			[1986TUR/KRA]

(a) Re-evaluated values, see Appendix A.

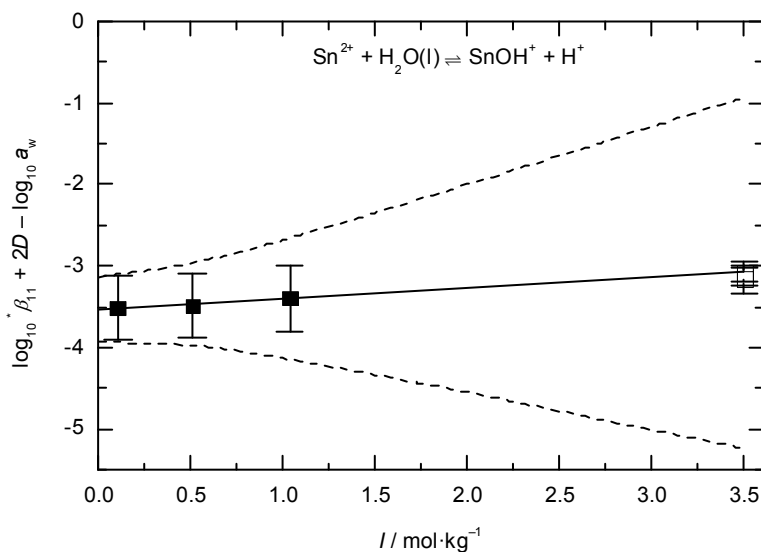
(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which quantities were used originally by the authors.



For Reaction (VII.2) remarkably consistent equilibrium constants are available for  $I = 3 \text{ M NaClO}_4$ , but conflicting data were published for lower ionic strengths. The constants reported in [1939GOR], [1941GAR/HEI] and [1952VAN/RHO] were rejected for reasons mentioned in Appendix A. Only the data reported by Pettine *et al.* can be used to determine the ionic strength dependence of  $\log_{10}^* \beta_{1,1}^0$ . However, these measurements were conducted in  $\text{NaNO}_3$  media, and Andreev *et al.* [1980AND/SAM] reported the formation of weak nitrate complexes of tin(II). Under the experimental conditions applied in [1981PET/MIL] such species were not detected by the authors. Moreover the experimental data reported by Pettine *et al.* cannot be re-evaluated correctly by considering the formation of nitrate complexes (see Appendix A). Therefore, the presence of  $\text{Sn}(\text{NO}_3)_x^{2-x}$  complexes were ignored in the re-evaluation performed by the reviewers, but the uncertainties of the resulting constants were increased, due to their possible presence. The extrapolation of the recalculated constants to zero ionic strength (Figure VII-1), assuming negligible variation between 20 and 25 °C, resulted in the selected value

$$\log_{10}^* \beta_{1,1}^0 ((\text{VII.2}), 298.15 \text{ K}) = - (3.53 \pm 0.40).$$

Figure VII-1: Extrapolation of the equilibrium constants for reaction  $\text{Sn}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SnOH}^+ + \text{H}^+$  recalculated from the data measured in  $\text{NaNO}_3$  media [1981PET/MIL]. The data for 3 M  $\text{NaClO}_4$  ( $\square$ ) were not included in the regression.



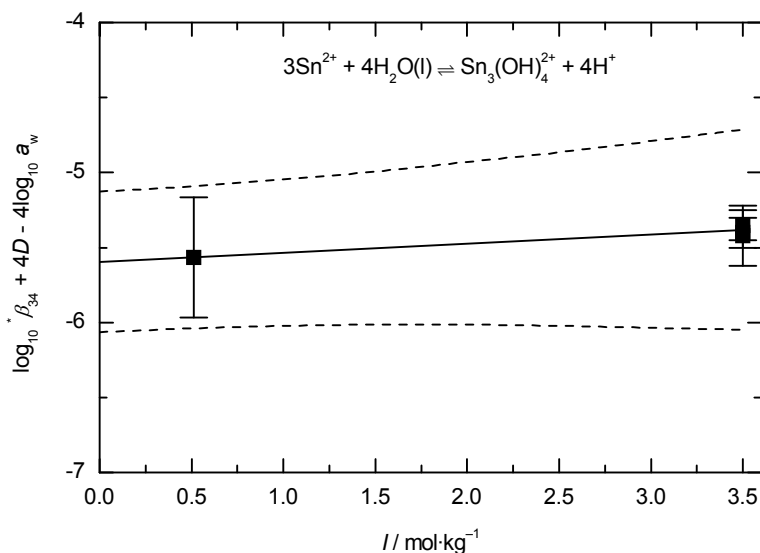
The corresponding ion interaction coefficient is  $\Delta\epsilon(\text{VII.2}), \text{NaNO}_3 = -(0.13 \pm 0.60) \text{ kg}\cdot\text{mol}^{-1}$ . Based on the selected  $\log_{10} {}^*\beta_{1,1}^0(\text{VII.2}), 298.15 \text{ K}$  and the constants determined for  $I = 3 \text{ M NaClO}_4$ ,  $\Delta\epsilon(\text{VII.2}), \text{NaClO}_4 = -(0.12 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  can be derived for perchlorate medium, which results in  $\epsilon(\text{SnOH}^+, \text{ClO}_4^-) = -(0.07 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$ .

The equilibrium constants reported for Reaction (VII.3) at  $I = 3.0 \text{ M NaClO}_4$  are in excellent agreement, but only a single value is available at lower ionic strength. Since the complex  $\text{Sn}_3(\text{OH})_4^{2+}$  is the dominant hydrolytic species at  $[\text{Sn}^{2+}]_{\text{tot}} > 0.1 \text{ mM}$ , it seems worthwhile to extrapolate these constants to zero ionic strength, despite the limited number of data. The weighted linear regression is shown on Figure VII-2. The resulting selected value is:

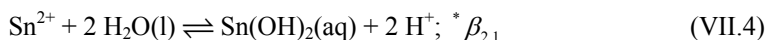
$$\log_{10} {}^*\beta_{4,3}^0(\text{VII.3}), 298.15 \text{ K} = -(5.60 \pm 0.47).$$

From the plot in Figure VII-2,  $\Delta\epsilon(\text{VII.3}), \text{NaClO}_4 = -(0.06 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$  can be derived, which corresponds to  $\epsilon(\text{Sn}_3(\text{OH})_4^{2+}, \text{ClO}_4^-) = -(0.02 \pm 0.16) \text{ kg}\cdot\text{mol}^{-1}$ .

Figure VII-2: Extrapolation of the equilibrium constants for reaction  $3\text{Sn}^{2+} + 4\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}_3(\text{OH})_4^{2+} + 4\text{H}^+$  determined in  $\text{NaClO}_4$  media.



In neutral and alkaline solutions the formation of two water soluble hydroxido complexes is generally recognised



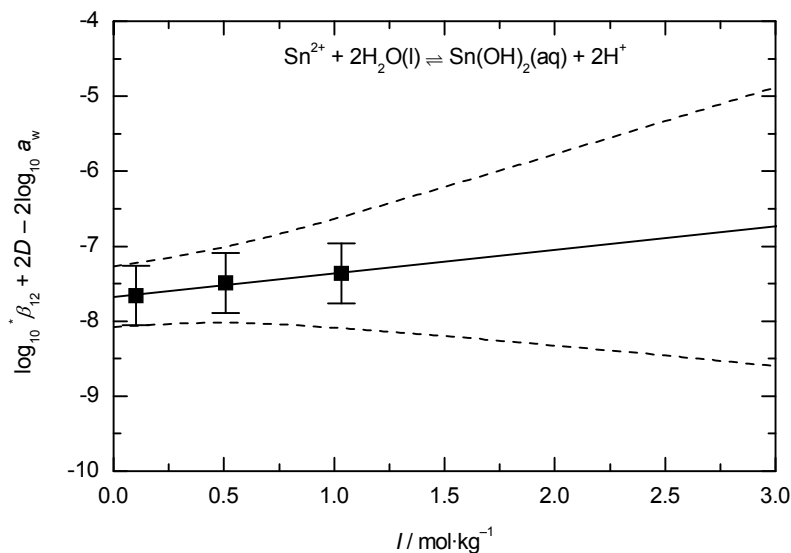


In the neutral pH range  $\text{Sn}(\text{OH})_2$  is the main species, which has very low solubility. The only reliable solution equilibrium study concerning this complex is reported by Pettine *et al.* [1981PET/MIL] using a very low tin(II) concentration ( $[\text{Sn}^{2+}]_{\text{tot}} = 5.4 \times 10^{-7} \text{ M}$ ). As mentioned above, the graphical data reported in [1981PET/MIL] were re-evaluated by the present review, neglecting the possible presence of nitrate complexes. The SIT analysis of the recalculated formation constants (Figure VII-3), assuming the temperature correction to 25 °C negligible, resulted in the selected value:

$$\log_{10} {}^* \beta_{2,1}^{\circ} (\text{VII.4}, 298.15 \text{ K}) = - (7.68 \pm 0.40)$$

and  $\Delta\alpha(\text{VII.4}, \text{NaNO}_3) = - (0.31 \pm 0.60) \text{ kg}\cdot\text{mol}^{-1}$ .

Figure VII-3: Extrapolation of the equilibrium constants for reaction  $\text{Sn}^{2+} + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_2(\text{aq}) + 2 \text{H}^+$  recalculated from the data measured in  $\text{NaNO}_3$  media [1981PET/MIL].



Five reliable reports are available for the equilibrium constant of Reaction (VII.5). The primary data related to the alkaline dissolution of  $\text{SnO}(\text{s})$  reported in [1941GAR/HEI] have been re-evaluated for the purposes of this review using the SIT, which resulted in  $\log_{10} {}^* K_3^{\circ} = (4.46 \pm 0.01)$  for the reaction (VII.6):



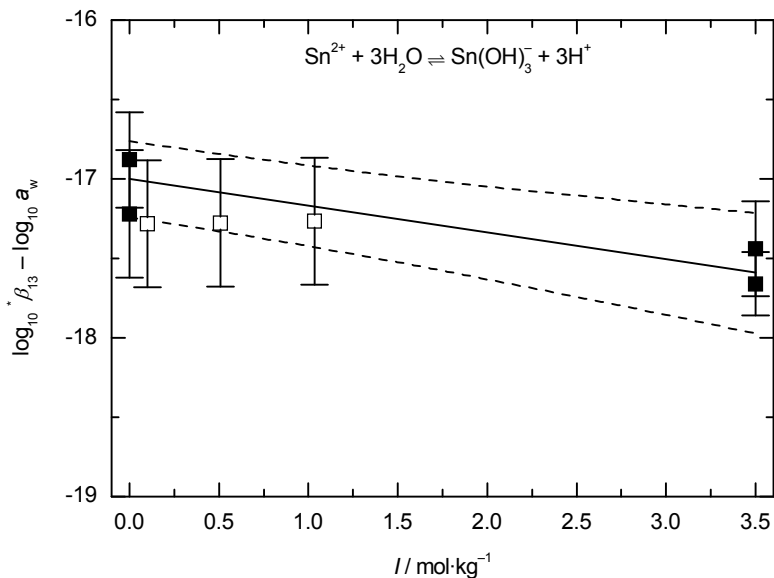
and  $\Delta\alpha(\text{VII.6}, \text{NaOH}) = (0.18 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ .

Using the value of  $\log_{10} {}^*K_3^0$ , the above selected  $\log_{10} {}^*\beta_{2,1}^0$  ((VII.4), 298.15 K) and  $\text{p}K_w^0 = 14.00$ ,  $\log_{10} {}^*\beta_{3,1}^0 = -(17.22 \pm 0.40)$  can be derived.

The SIT analysis of the latter value and those reported in [1977MAR], [1977SMI/KRA] and [1978DIC/LOT] resulted in the selected constant (Figure VII-4)

$$\log_{10} {}^*\beta_{3,1}^0 \text{ ((VII.5), 298.15 K)} = -(17.00 \pm 0.60).$$

Figure VII-4: Extrapolation of the equilibrium constants for reaction  $\text{Sn}^{2+} + 3 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_3^- + 3 \text{H}^+$  determined in  $\text{NaClO}_4$  media (solid squares). The data for  $\text{NaNO}_3$  media, recalculated from [1981PET/MIL] (open squares) were not included in the regression.



The calculated uncertainty ( $\pm 0.24$ ) was increased to cover the value extrapolated to  $I = 0$  using the re-evaluated equilibrium constants from [1981PET/MIL] ( $\log_{10} {}^*\beta_{3,1}^0 = -(17.56 \pm 0.40)$ ). From the slope of the straight line in Figure VII-4  $\Delta\alpha(\text{VII.5}, \text{NaClO}_4) = (0.21 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$  can be calculated, which corresponds to  $\alpha(\text{Na}^+, \text{Sn}(\text{OH})_3^-) = -(0.01 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ . This ion interaction coefficient can also be obtained from  $\Delta\alpha(\text{VII.6}, \text{NaOH})$  (see above). The calculation based on the data of [1941GAR/HEI] results in  $\alpha(\text{Na}^+, \text{Sn}(\text{OH})_3^-) = (0.22 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , which seems to be more reliable than the above value.

The selected thermodynamic formation constants correspond to:

$$\begin{aligned}\Delta_r G_m^\circ ((\text{VII.2}), 298.15 \text{ K}) &= (20.1 \pm 2.3) \text{ kJ mol}^{-1}, \\ \Delta_r G_m^\circ ((\text{VII.3}), 298.15 \text{ K}) &= (32.0 \pm 2.7) \text{ kJ mol}^{-1}, \\ \Delta_r G_m^\circ ((\text{VII.4}), 298.15 \text{ K}) &= (43.8 \pm 2.3) \text{ kJ mol}^{-1}, \\ \Delta_r G_m^\circ ((\text{VII.5}), 298.15 \text{ K}) &= (97.0 \pm 3.4) \text{ kJ mol}^{-1}.\end{aligned}$$

The selected Gibbs energies of formation are:

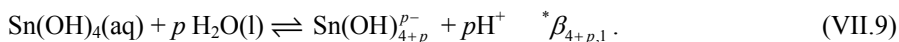
$$\begin{aligned}\Delta_f G_m^\circ (\text{SnOH}^+, 298.15 \text{ K}) &= -(244.4 \pm 2.3) \text{ kJ mol}^{-1}, \\ \Delta_f G_m^\circ (\text{Sn}_3(\text{OH})_4^{2+}, 298.15 \text{ K}) &= -(998.8 \pm 2.8) \text{ kJ mol}^{-1}, \\ \Delta_f G_m^\circ (\text{Sn}(\text{OH})_2(\text{aq}), 298.15 \text{ K}) &= -(457.8 \pm 2.3) \text{ kJ mol}^{-1}.\end{aligned}$$

Reaction (VII.5) leads to  $\Delta_f G_m^\circ (\text{Sn}(\text{OH})_3^-, 298.15 \text{ K}) = -(641.8 \pm 3.41) \text{ kJ mol}^{-1}$  which overlaps with the selected value of  $-(645.01 \pm 0.77) \text{ kJ mol}^{-1}$ , see Section VII.2.2.3.

## VII.1.2 Tin(IV) hydroxido complexes

Only a single experimental study is available for the hydrolysis of tin(IV) under acidic conditions (Table VII-2). Nazarenko *et al.* investigated the hydrolytic reactions of tin(IV) by a spectrophotometric method using salicylfluorone as competing ligand [1971NAZ/ANT]. The reported data indicate, that tin(IV) strongly hydrolyses in aqueous solution, even below pH 1.2. The formation of the sparingly soluble  $\text{Sn}(\text{OH})_4$  is complete at pH 2. Since several experimental details in [1971NAZ/ANT] are disputable (see Appendix A), we agree with the conclusion of [1999LOT/OCH] and [2002HUM/BER], that the values reported by Nazarenko *et al.* are only estimates. Therefore, formation constants for the complexes  $\text{SnOH}^{3+}$ ,  $\text{Sn}(\text{OH})_2^{2+}$  and  $\text{Sn}(\text{OH})_3^+$  cannot be selected.

Five reports are available for the solubility of  $\text{SnO}_2(\text{s})$  in alkaline solutions at temperatures relevant for the present review [1970KUR/BAR], [1970BAR/KLI], [1973KLI/BAR], [1997AMA/CHI] and [1998ODA/AMA], see Table VII-2. To describe the formation of hydroxido complexes in alkaline pH, the solubility equilibria of crystalline and amorphous  $\text{SnO}_2$  have been used:



The solubilities of crystalline as well as amorphous tin dioxide remain constant between  $1.9 < \text{pH} < 8$ .

$$\log_{10} K_{s,0}^{\circ}(\text{SnO}_2, \text{cr}, 298.15 \text{ K}) = -(8.06 \pm 0.11)$$

$$\log_{10} K_{s,0}^{\circ}(\text{SnO}_2, \text{am}, 298.15 \text{ K}) = -(7.22 \pm 0.08).$$

Table VII-2: Experimental equilibrium data for the hydrolysis of tin(IV).

Method	Ionic media	$t/^{\circ}\text{C}$	$\log_{10} \beta_p$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn(OH)}_4(\text{aq}) + 4 \text{H}^+ \rightleftharpoons \text{Sn}^{4+} + 4 \text{H}_2\text{O(l)}$						
sp	1 M (H/K)NO <sub>3</sub>	25	-0.17 <sup>(c)</sup>			[1971NAZ/ANT]
$\text{Sn(OH)}_4(\text{aq}) + 3 \text{H}^+ \rightleftharpoons \text{Sn(OH)}_3^+ + 3 \text{H}_2\text{O(l)}$						
sp	1 M (H/K)NO <sub>3</sub>	25	0.66 <sup>(c)</sup>			[1971NAZ/ANT]
$\text{Sn(OH)}_4(\text{aq}) + 2 \text{H}^+ \rightleftharpoons \text{Sn(OH)}_2^{2+} + 2 \text{H}_2\text{O(l)}$						
sp	1 M (H/K)NO <sub>3</sub>	25	1.04 <sup>(c)</sup>			[1971NAZ/ANT]
$\text{Sn(OH)}_4(\text{aq}) + \text{H}^+ \rightleftharpoons \text{Sn(OH)}_3^+ + \text{H}_2\text{O(l)}$						
sp	1 M (H/K)NO <sub>3</sub>	25	0.97 <sup>(c)</sup>			[1971NAZ/ANT]
$\text{Sn(OH)}_4(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{Sn(OH)}_5^- + \text{H}^+$						
sol	→ 0 (NaOH)	25	-12.4	-11.28 ± 0.09		[1970BAR/KLI]
sol	0.1 M NaClO <sub>4</sub>	25	-7.75	-8.38 ± 0.25	-8.38 ± 0.30	[1997AMA/CHI]
	→ 0		-7.97	-8.60 ± 0.30	-8.60 ± 0.40	[1998ODA/AMA]
$\text{Sn(OH)}_4(\text{aq}) + 2 \text{H}_2\text{O(l)} \rightleftharpoons \text{Sn(OH)}_6^{2-} + 2 \text{H}^+$						
sol	→ 0 (NaOH)	200	-20.2 <sup>(d)</sup>	-20.16 ± 0.20 <sup>(d)</sup>		[1973KLI/BAR]
sol	0.1 M NaClO <sub>4</sub>	25	-17.74	-18.01 ± 0.11	-18.01 ± 0.20	[1997AMA/CHI]
	→ 0		-18.38	-18.67 ± 0.15	-18.67 ± 0.30	[1998ODA/AMA]

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which quantities were used originally by the authors.

(c) Using  $\text{p}K_w = 13.74$  for  $I = 1 \text{ M KNO}_3$ .

(d) Using  $\text{p}K_w = 11.2$  for  $I = 0$  and  $T = 200 \text{ }^{\circ}\text{C}$ .

These values were selected and correspond to  $\Delta_f G_m^{\circ}(\text{SnO}_2, \text{am}, 298.15 \text{ K}) = -(511.87 \pm 0.78) \text{ kJ mol}^{-1}$  and  $\Delta_f G_m^{\circ}(\text{Sn(OH)}_4, \text{aq}, 298.15 \text{ K}) = -(944.93 \pm 0.66)$ .

The dissolution of  $\text{SnO}_2(\text{s})$  above pH 8 was explained by the formation of either  $\text{Sn(OH)}_5^-$  [1970BAR/KLI], or  $\text{Sn(OH)}_6^{2-}$  [1973KLI/BAR], as well as by the presence of both species [1970KUR/BAR], [1997AMA/CHI], [1998ODA/AMA]. The hydrolysis constants reported in [1970KUR/BAR] for  $T = 373 \text{ K}$  were later considered as unreliable by the authors themselves [1973KLI/BAR], since the equilibration time was too short to reach the equilibrium. The experimental methods applied in [1997AMA/CHI] and [1998ODA/AMA] (radiometry using  $^{113}\text{Sn}$  and ICP-MS (inductively coupled plasma mass spectrometry)) allowed much higher precision than

that used in [1970BAR/KLI] and [1973KLI/BAR] (colorimetry), therefore in this review the former reports were used to derive selected values. The experimental data reported in [1997AMA/CHI] and later [1998ODA/AMA] for the solubility of crystalline and amorphous SnO<sub>2</sub> at  $I \approx 0.01$  and 0.1 M, respectively, including both under- and oversaturation measurements, were re-evaluated for the purposes of this review (see Figure VII-5). The resulting constants (see Table VII-2 and Appendix A) were extrapolated to  $I = 0$  using SIT, assuming  $\Delta\varepsilon$  (VII.9),  $p = 1$  and 2)  $\approx (0 \pm 0.3)$  kg·mol<sup>-1</sup>. Since in [1997AMA/CHI] and [1998ODA/AMA] low ionic strength was applied ( $I \approx 0.1$  M), the above assumption introduces nearly negligible uncertainties to the thermodynamic formation constants ( $\Delta\varepsilon \times I_m = (0 \pm 0.3) \times 0.1 = \pm 0.03$ ). This extrapolation resulted in the selected values of

$$\log_{10} K_{s,0}^{\circ} \text{ ((VII.7), 298.15 K)} = - (8.06 \pm 0.11)$$

$$\log_{10} K_{s,0}^{\circ} \text{ ((VII.8), 298.15 K)} = - (7.22 \pm 0.08)$$

$$\log_{10} {}^* \beta_{5,1}^{\circ} \text{ ((VII.9), } p = 1, 298.15 \text{ K)} = - (8.60 \pm 0.40)$$

$$\log_{10} {}^* \beta_{6,1}^{\circ} \text{ ((VII.9), } p = 2, 298.15 \text{ K)} = - (18.67 \pm 0.30).$$

The uncertainties are assigned by the reviewers, reflecting both the experimental errors (see Appendix A) and the neglected  $\Delta\varepsilon$  values.

The solubility of SnO<sub>2</sub> determined in [1973KLI/BAR] at 200 °C (Table VII-2) can be used as an estimate at this temperature.

The above selected thermodynamic constants correspond to:

$$\Delta_r G_m^{\circ} \text{ ((VII.7), 298.15 K)} = (46.01 \pm 0.63) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^{\circ} \text{ ((VII.8), 298.15 K)} = (41.21 \pm 0.46) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^{\circ} \text{ ((VII.9), } p = 1, 298.15 \text{ K)} = (49.1 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^{\circ} \text{ ((VII.9), } p = 2, 298.15 \text{ K)} = (106.6 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}.$$

The selected Gibbs energies of formation are:

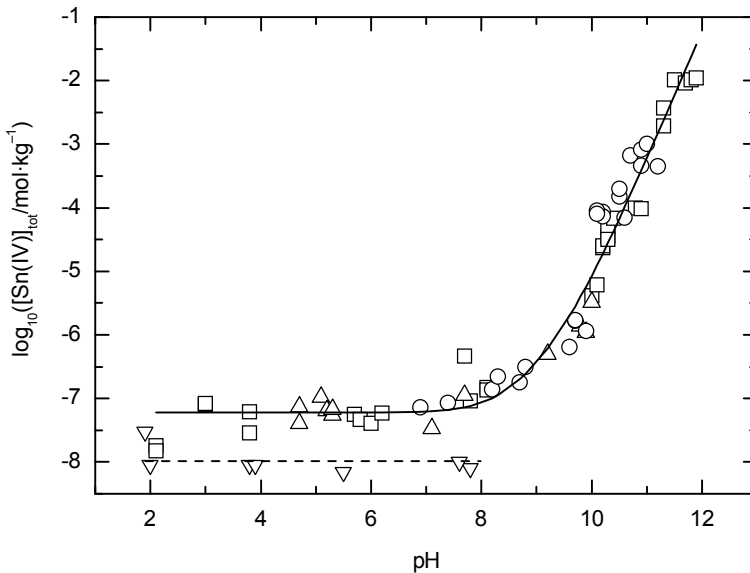
$$\Delta_f G_m^{\circ} \text{ (SnO}_2, \text{ am, 298.15 K)} = - (511.87 \pm 0.78) \text{ kJ mol}^{-1},$$

$$\Delta_f G_m^{\circ} \text{ (Sn(OH)}_4, 298.15 \text{ K)} = - (944.93 \pm 0.66) \text{ kJ mol}^{-1},$$

$$\Delta_f G_m^{\circ} \text{ (Sn(OH)}_5^-, 298.15 \text{ K)} = - (1133.0 \pm 2.4) \text{ kJ mol}^{-1},$$

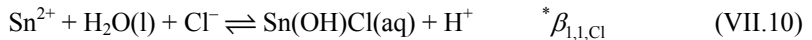
$$\Delta_f G_m^{\circ} \text{ (Sn(OH)}_6^{2-}, 298.15 \text{ K)} = - (1312.6 \pm 1.8) \text{ kJ mol}^{-1}.$$

Figure VII-5: Solubility of crystalline and amorphous  $\text{SnO}_2$  as the function of pH in 0.1 M  $\text{NaClO}_4$  solution, based on the experimental data reported in [1997AMA/CHI] and [1998ODA/AMA] ( $\square$ : selected experimental data for  $\text{SnO}_2(\text{am})$ ;  $\nabla$ : selected experimental data for  $\text{SnO}_2(\text{cr})$  [1997AMA/CHI];  $\triangle$ : oversaturation experiments [1998ODA/AMA];  $\circ$ : undersaturation experiments; solid line: obtained for  $\text{SnO}_2(\text{am})$  using the re-evaluated values  $\log_{10} K_{s,0} = -(7.22 \pm 0.08)$ ,  $\log_{10} {}^* \beta_{5,1} = -(8.38 \pm 0.25)$  and  $\log_{10} {}^* \beta_{6,1} = -(18.01 \pm 0.11)$  (see Appendix A); dashed line: obtained for  $\text{SnO}_2(\text{cr})$  using the re-evaluated value  $\log_{10} K_{s,0} = -(8.06 \pm 0.11)$ ).



### VII.1.3 Mixed hydroxido complexes of tin(II)

The  $\log_{10} {}^* \beta_{1,1}$  values obtained in  $\text{NaCl}$  media [1981PET/MIL], [1995DJU/JEL] are considerably higher than those determined in  $\text{NaNO}_3$  or  $\text{NaClO}_4$  solutions (see Table VII-1). The difference is probably related to the formation of  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$ .



The value of  ${}^* \beta_{1,1,\text{Cl}}$  is related to  ${}^* \beta_{1,1}$  determined in  $\text{NaCl}$  and in non-coordinating background electrolytes ( $\text{NaClO}_4/\text{NaNO}_3$ ):

$${}^* \beta_{1,1}(\text{NaCl}) \approx {}^* \beta_{1,1}(\text{NaClO}_4/\text{NaNO}_3) + {}^* \beta_{1,1,\text{Cl}}.$$

Using the above relationship,  $\log_{10} {}^* \beta_{1,1,\text{Cl}} \approx -3.2$  (0.5 M  $\text{NaCl}$ ) and  $\approx -2.2$  (3 M  $\text{NaCl}$ ) can be derived from the data of [1981PET/MIL] and [1995DJU/JEL], respectively. However, the high uncertainty of the constants reported in [1995DJU/JEL]



(see Appendix A) does not allow to estimate reliably the thermodynamic equilibrium constant for Reaction (VII.10).

### VII.1.4 Mixed hydroxido complexes of tin(IV)

Qualitative data on the formation of  $\text{SnCl}_5\text{OH}^{2-}$ ,  $\text{SnCl}_4(\text{OH})_2^{2-}$ ,  $\text{SnCl}_3(\text{OH})_3^{2-}$  and  $\text{SnCl}_2(\text{OH})_4^{2-}$  detected by Mössbauer spectroscopy are reported in [1991KHR/ZAP]. In [1983CHE/DID] the formation of  $\text{SnF}_5\text{OH}^{2-}$  was detected by  $^{19}\text{F}$  NMR spectroscopy. Thermodynamic data are reported for mixed hydroxido complexes of tin(IV) in [1968DEA/EVA], [1970KUR/MAR] and [1975KLI/BAR]. The increased solubility of amorphous  $\text{SnO}_2$  in NaF or HF solutions, as compared to pure water, was explained by the formation of the complexes  $\text{Sn}(\text{OH})_{4-n}\text{F}_n(\text{aq})$  and  $\text{Sn}(\text{OH})_4\text{F}_n^{n-}$  ( $n = 1$  at 25 and 50 °C,  $n = 2$  at 200 °C, see Appendix A) [1975KLI/BAR]. Based on their  $^{19}\text{F}$  NMR measurements, Dean and Evans [1968DEA/EVA] reported  $\log_{10} K = 5.1$  for the equilibrium constant of the reaction  $\text{SnF}_6^{2-} + \text{OH}^- \rightleftharpoons \text{SnF}_5\text{OH}^{2-} + \text{F}^-$ . Due to the reasons mentioned in Appendix A, none of the reported constants can be used to derive selected values.

## VII.2 Solid tin oxides and hydroxides

### VII.2.1 Introduction

There is only one stable tin(II) hydroxide which can be described as tin(II) hydroxide oxide [1961DON/MOS]. Single crystals suitable for X-ray analysis of this material were obtained and the structural formula was determined to be  $\text{Sn}_6\text{O}_4(\text{OH})_4$  [1968HOW/MOS]. This phase occurs in nature as a corrosion product of elemental tin and has been named hydromarchite [1971ORG/MAN], [1973HOW/MOS]. So far no information on thermodynamic properties of  $\text{Sn}_6\text{O}_4(\text{OH})_4$ , qualifying for selection in this review, is available.

Tin(II) oxide exists in several modifications. The thermodynamically stable form at 298.15 K and  $10^5$  Pa is blue-black tetragonal SnO, which is the only example for a regular square-pyramidal tin(II) coordination [1980PAN/DEN]. The name of the naturally occurring mineral is romarchite, a pewter artefact [1971ORG/MAN], [2003DUN/CRA].

Donaldson *et al.* [1961DON/MOS2] established the conditions under which the metastable red orthorhombic modification can be prepared. A second red SnO was prepared by Kwestroo and Vromans [1967KWE/VRO]. There is no systematic thermodynamic investigation for the red tin(II) oxide phases, therefore, only values for blue-black tetragonal SnO have been selected in this review.

Tin(II) oxide decomposes at ambient pressure at temperatures above 500 K into metallic tin and an intermediate tin oxide either according to disproportionation Reactions (VII.11) and (VII.12) [1947SPA/KOH]



or according to disproportionation Reactions (VII.13) and (VII.14) [1973MUR/TRO]



The intermediate reaction products could not be separated as pure phases due to their nano-crystalline nature. As indicated by Reactions (VII.11) and (VII.13) the stoichiometry of the intermediate phase is still under discussion.  $\text{Sn}_3\text{O}_4$ ,  $\text{Sn}_2\text{O}_3$ ,  $\text{Sn}_2\text{O}_6$  or  $\text{Sn}_5\text{O}_8$  are considered as possible intermediates [2005GIE/POR], [2008SEK/TOG], [2010TAN/SEK]. A first structural study by electron diffractometry yielded a triclinic unit cell for a suggested stoichiometry  $\text{Sn}_3\text{O}_4$  [1967LAW]. From a recent precession electron diffraction study [2010WHI/MOR] the complete crystal structure was derived confirming the unit cell of [1967LAW] and the epitaxial relationships between the various oxide structures of tin. From coulometric titrations in a high-temperature galvanic cell Yang *et al.* [1994YAN/SUI] derived a temperature function for the Gibbs energy of formation of  $\text{Sn}_3\text{O}_4$ , which was used subsequently in phase diagram modeling of the system  $\text{SnO-SnO}_2$  [2003CAH/DAV]. Although stoichiometry and structure of the elusive intermediate tin oxides  $\text{Sn}_3\text{O}_4$  and  $\text{Sn}_2\text{O}_3$  have been studied and an attempt was made to ascertain thermodynamic properties of  $\text{Sn}_3\text{O}_4$ , the latter do not qualify for selection of standard values in this review.

$\text{SnO}_2$  occurs naturally as the mineral cassiterite and is the main ore of tin. Cassiterite has the rutile-type structure [1964WYC] (tetragonal, space group  $P4(2)/mmm$ ,  $a = 4.7373 \text{ \AA}$ ,  $c = 3.1864 \text{ \AA}$ ,  $Z = 2$ , unit cell volume =  $71.51 \text{ \AA}^3$ ). Cassiterite dissolves easily in alkali hydroxides; from these solutions brucite like hydroxides such as  $\text{K}_2\text{Sn}(\text{OH})_6$  [1976HON/ZUC] can be crystallised. Double oxides may form by combination of  $\text{K}_2\text{O}$  and  $\text{SnO}_2$  ( $\text{K}_4\text{SnO}_4$ ,  $\text{K}_2\text{Sn}_3\text{O}_7$  and  $\text{K}_2\text{SnO}_3$ ). A mixed valence oxide  $\text{Sn}_3\text{O}_4$  has also been reported [1984GRE/EAR]. The structure is triclinic with space group  $P1(2)$  and  $V_{\text{cell}} = 233.56 \text{ \AA}^3$ .

## VII.2.2 SnO(cr)

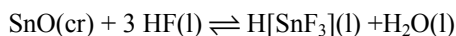
### VII.2.2.1 Enthalpy of formation of SnO(cr)

Humphrey and O'Brien [1953HUM/OBR] determined the enthalpy of formation of  $\text{SnO}(\text{cr})$  comparatively early. They obtained a value of  $\Delta_f H_m^\circ(\text{SnO}, \text{cr}, 298.15 \text{ K}) = -(286.00 \pm 1.34) \text{ kJ}\cdot\text{mol}^{-1}$  from the heat of combustion of tin.

Hirayama [1964HIR] stated that the entropy of this compound is reported (source unknown) to be  $(56.5 \pm 1.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . If we use the value of  $S_m^\circ(\text{Sn, cr, white, 298.15 K}) = (51.18 \pm 0.08) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  selected in this review, and the CODATA value for oxygen as  $(205.152 \pm 0.005) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , the calculated entropy of formation is  $-97.26 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and the resulting  $\Delta_f G_m^\circ$  is  $-257.00 \text{ kJ}\cdot\text{mol}^{-1}$ . Humphrey and O'Brien's value for the enthalpy of formation ( $-286.00 \text{ kJ}\cdot\text{mol}^{-1}$ ) differs considerably from the value measured by Lavut *et al.* [1981LAV/TIM] who determined the enthalpy of formation of SnO(cr) as:  $\Delta_f H_m^\circ(\text{SnO, tetragonal, 298.15 K}) = -(280.71 \pm 0.21) \text{ kJ}\cdot\text{mol}^{-1}$ . They used a well characterised sample in combustion calorimetry, the same method as used in [1953HUM/OBR]. The enthalpy of SnO(cr) differs from that reported in [1953HUM/OBR] significantly by almost 2%. The large discrepancy between the combustion calorimetric results cannot be resolved by looking at only these two sets of data. Arguments favouring the data by Lavut *et al.* [1981LAV/TIM] are based on a) high purity tin specimens, b) a reliable method of determining the reaction completeness, and c) a higher degree of combustion of tin. Lavut *et al.* also question the presence of water in gas form in the bomb which was not accounted for by Humphrey and O'Brien.

A quite thorough review of the available data ([1978COX], [1979GLU/MED], [1982WAG/EVA], [1982PAN]) was provided by Lamoreaux and Hildenbrand [1987LAM/HIL]. Their recommended values for  $\Delta_f H_m^\circ(\text{SnO, cr, 298.15 K})$  and  $S_m^\circ(\text{SnO, cr, 298.15 K})$  are  $-(280.681 \pm 0.166) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(57.167 \pm 0.291) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  respectively. The value of the enthalpy of formation of SnO(cr) is found to be consistent with the evaluation by [1979GLU/MED], [1978COX] and [1982PAN] but different from [1982WAG/EVA]. The entropy value is as in [1979GLU/MED] but different from others.

Solov'ev *et al.* [2001SOL/VLA] measured the enthalpies of reactions of SnO(cr) and SnF<sub>2</sub>(cr) with hydrofluoric acid in an isothermic-shell calorimeter. They used the reaction:



and obtained a value of  $-(67.2 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$  for the enthalpy of reaction but did not complete the thermochemical cycle to get the data for  $\Delta_f H_m^\circ(\text{SnO, cr, 298.15 K})$ .

The data of [1981LAV/TIM] and two critical reviews [1987LAM/HIL] and [1991GUR/VEY] support the higher value of enthalpy, while the dataset of Humphrey and O'Brien [1953HUM/OBR] using the same calorimetric method favours the lower value. There are two other determinations of enthalpy, one by Maier [1929MAI] who measured the potentials of galvanic cells and obtained  $-(285.4 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$  and the second by Garrett and Heiks [1941GAR/HEI] who used solubility measurements and obtained  $-(283.9 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$ . It will be shown in Section VII.2.2.4 that the data of [1981LAV/TIM] cannot be taken into account for the evaluation of  $\Delta_f H_m^\circ(\text{SnO, cr, 298.15 K})$ .

### VII.2.2.2 Heat capacity of SnO(cr)

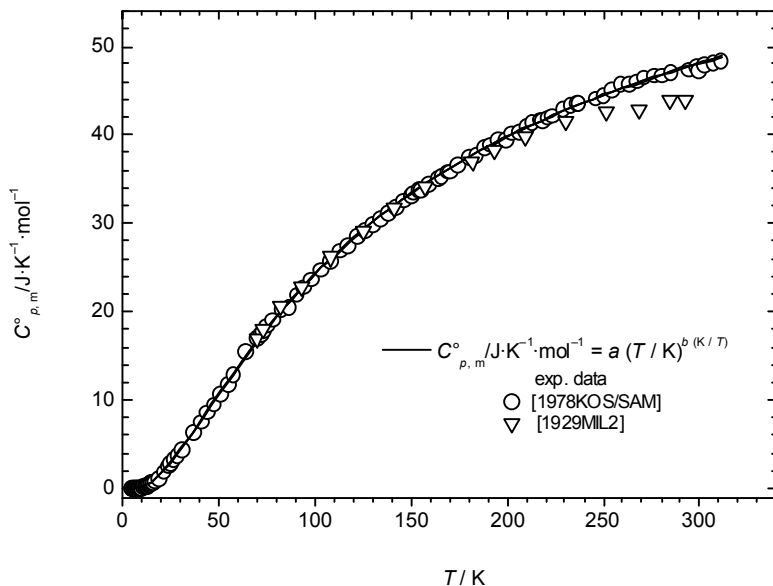
Kostruykov *et al.* [1978KOS/SAM] made 120 measurements of the heat capacity of SnO(cr) from a temperature of 4.3 to 310.7 K (Table A-37), and determined the enthalpy ( $H_T - H_{0K}$ ) and entropy (1978KOS/SAM). The SnO sample was a blue-black modification (tetragonal system SG  $P4/nmn$ , structural type PbO) as revealed by X-ray analysis. The heat capacity of SnO(cr) from 70 to 293 K was also reported by Millar [1929MIL2].

The experimental data of [1978KOS/SAM] on the heat capacity of SnO(cr) were extrapolated to  $T = 0$  by Debye's  $T^{-3}$  law. From  $T = 4.3$  to 312 K, the coefficients of a modified exponential power function

$$C_{p,m}^{\circ}(\text{SnO, cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 77.816 \times (T/\text{K})^{-25.295(K/T)} \quad (\text{VII.15})$$

were fitted to the data (see Figure VII-6).

Figure VII-6: Standard molar heat capacity of tetragonal tin(II) oxide (○: experimental data of [1978KOS/SAM]; △: experimental data of [1929MIL2]).



Equation (VII.15) leads to  $C_{p,m}^{\circ}(\text{SnO, cr}, 298.15 \text{ K}) = 47.989 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The value obtained by [1978KOS/SAM] is  $47.781 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . These authors arrived at a

similar result ( $47.756 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) by linear regression of  $C_{p,m}^{\circ}$  between 263 and 311 K, see Appendix A on [1978KOS/SAM].

From  $T \approx 250 \text{ K}$  upwards the heat capacities of SnO(cr) measured by [1929MIL2] deviate increasingly from those of [1978KOS/SAM] and thus were not considered in this review.

The entropy may be calculated by integrating  $(C_{p,m}^{\circ}/T)$  with respect to  $T$  where  $C_{p,m}^{\circ}$  is given by Eq.(VII.15), but the coefficients of Eq. (VII.15) were slightly modified by non linear regression of data  $T$ ,  $C_{p,m}^{\circ}/T$ , see Appendix A entry on [1978KOS/SAM].

$$\begin{aligned} S_m^{\circ}(\text{SnO, cr, 298.15 K}) &= C_{p,m}^{\circ}(4.281 \text{ K})/3 + \int_{4.281\text{K}}^{298.15\text{K}} (C_{p,m}^{\circ}/T)dT \\ &= (57.180 \pm 0.220) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}. \end{aligned}$$

This value of the entropy overlaps with the value of  $(57.17 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  given by [1978KOS/SAM] and the CODATA key value  $(57.17 \pm 0.30) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [1989COX/WAG].

### VII.2.2.3 Solubility of SnO(cr)

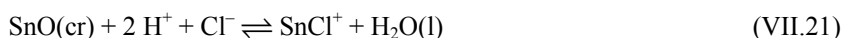
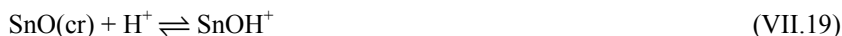
The determination of the solubility constant of SnO(cr) in aqueous solutions, such as defined by Eq. (VII.16), is in principle a straightforward method and can be used to evaluate the standard Gibbs energy of formation,  $\Delta_f G_m^{\circ}(\text{SnO, cr, 298.15 K})$ , of the solid SnO phase.



$$\Delta_{\text{sol}} G_m^{\circ}(\text{VII.16}) = -RT \cdot \log_{10} {}^* K_{s_0}^{\circ} \quad (\text{VII.17})$$

$$\Delta_f G_m^{\circ}(\text{SnO, cr}) = \Delta_f G_m^{\circ}(\text{Sn}^{2+}) + \Delta_f G_m^{\circ}(\text{H}_2\text{O, l}) - \Delta_{s,\text{in}} G_m^{\circ}(\text{VII.16}) \quad (\text{VII.18})$$

In the case of solubility studies on SnO(cr) complications arise, because  $\text{Sn}^{2+}$  forms hydroxido complexes such as  $\text{SnOH}^+$  and  $\text{Sn}_3(\text{OH})_4^{2+}$  at comparatively low pH values as well as chlorido complexes at rather low chloride concentrations. Thus reactions described by Eqs. (VII.19) to (VII.21) will contribute to the dissolution process even in the acidic range.

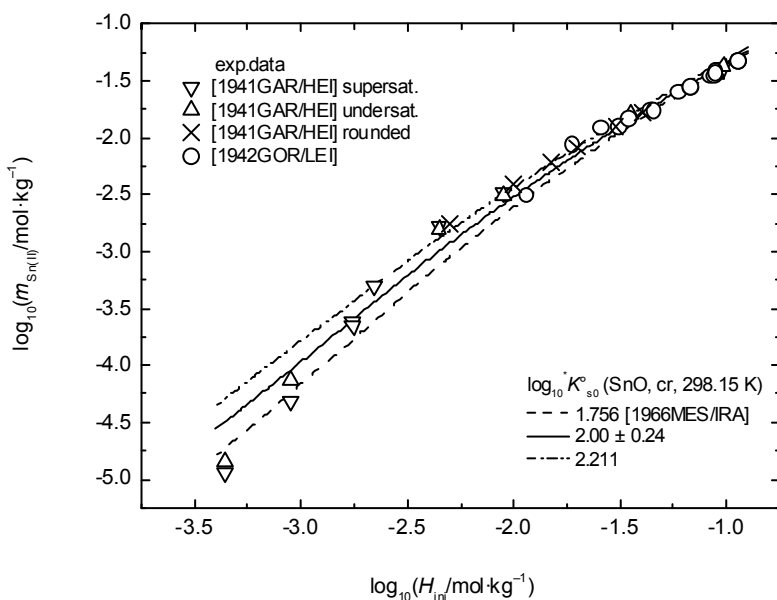


There are only three solubility studies which report data useful for the evaluation of  $\Delta_f G_m^{\circ}(\text{SnO, cr})$ : [1941GAR/HEI], [1942GOR/LEI] and [1966MES/IRA].

Garrett and Heiks [1941GAR/HEI] equilibrated SnO(s) in dilute HCl solutions. An attempt was made to approach equilibrium from supersaturation and

undersaturation, see discussion in the respective Appendix A entry. In Figure VII-7 the logarithms of the experimentally observed values of the total molality of Sn(II),  $m_{\text{Sn(II)}}$ , and the initial molality of HCl,  $H_{\text{ini}}$ , were plotted against each other. As neither the molality of free  $\text{Sn}^{2+}$  nor the pH value has been determined, the estimated scatter amounts to at least  $\pm 0.24 \log K$  units. Thus the re-evaluation of the data of Garrett and Heiks taking into account all possible hydroxido and chlorido complexes results in  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -(253.29 \pm 1.38) \text{ kJ}\cdot\text{mol}^{-1}$ .

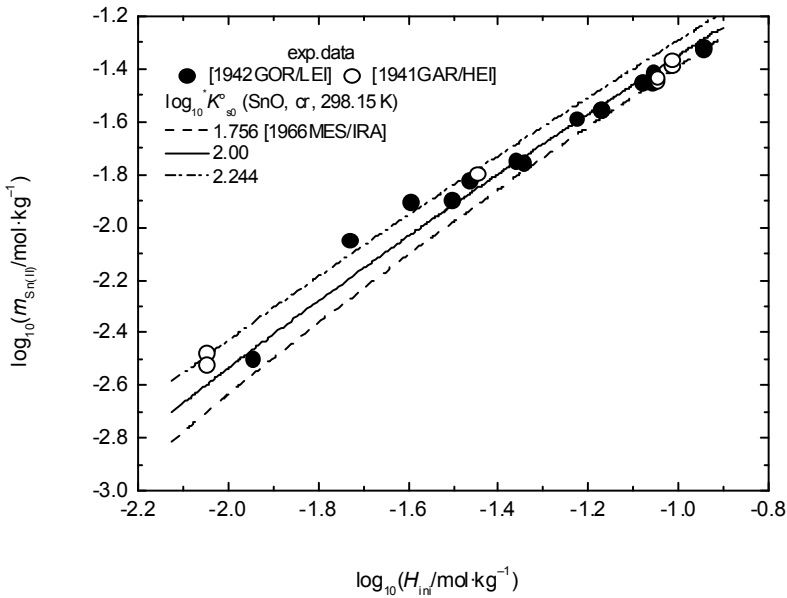
Figure VII-7: Solubility of SnO(cr) in HCl solution at 25 °C ( $\nabla$ : supersaturation experiments;  $\triangle$ : undersaturation experiments;  $\times$ : rounded values [1941GAR/HEI];  $\circ$ : experimental data [1942GOR/LEI]; solid line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -253.11 \text{ kJ}\cdot\text{mol}^{-1}$  [1941GAR/HEI]; dashed line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -254.51 \text{ kJ}\cdot\text{mol}^{-1}$ ; dash dotted line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -251.91 \text{ kJ}\cdot\text{mol}^{-1}$ ).



Gorman and Leighton [1942GOR/LEI] repeated the solubility study of [1941GAR/HEI] using commercially available SnO(cr) (C. P. from Baker) as solid and dilute perchloric acid, to avoid chlorido complex formation, as solvent. The experimental data were equilibrium concentration of Sn(II) total,  $m_{\text{Sn(II)}}$ , and initial  $\text{HClO}_4$  concentration,  $H_{\text{ini}}$ , again no pH values were measured. For comparison their data were recalculated to the molal basis. Figure VII-8 shows that the data of

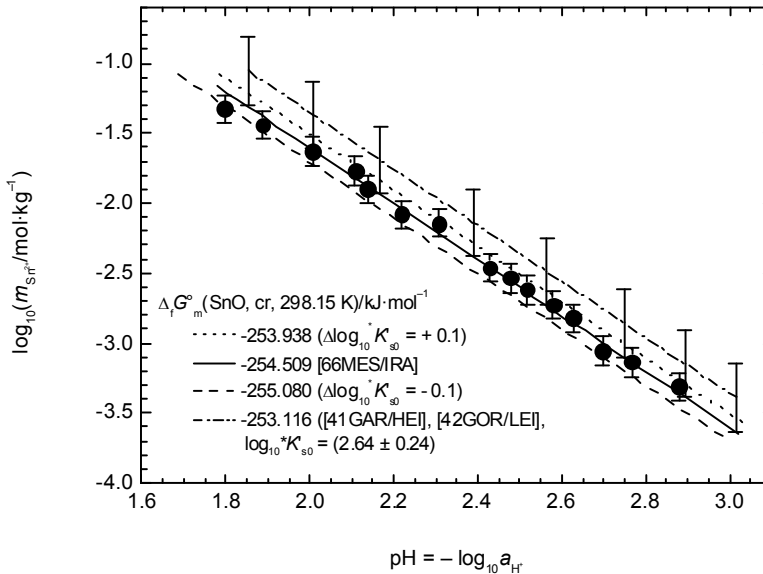
[1941GAR/HEI] and [1942GOR/LEI] agree quite well with each other, but the result is not very precise.

Figure VII-8: Solubility of SnO(cr) in HClO<sub>4</sub> solutions (●: experimental data of [1942GOR/LEI]; ○: experimental data of [1941GAR/HEI] (HCl); solid line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -253.11 \text{ kJ}\cdot\text{mol}^{-1}$  (this evaluation); dashed line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -254.509 \text{ kJ}\cdot\text{mol}^{-1}$  [1966MES/IRA]; dash dotted line:  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -251.72 \text{ kJ}\cdot\text{mol}^{-1}$ ).



Mesmer and Irani [1966MES/IRA] studied the solubility of high purity SnO(cr) purchased from Baker and Adamson. These authors kept the ionic strength constant (1.0 M NaClO<sub>4</sub>) and measured the pH values of the equilibrated solutions. As shown in Figure VII-9 a far more precise  $\log_{10} K_{s0}^\circ$  value was obtained ( $\log_{10} K_{s0}^\circ = 1.756 \pm 0.100$ ). Surprisingly enough the standard Gibbs energy of tin(II) oxide according to Mesmer and Irani's solubility data is considerably more negative  $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -(254.51 \pm 0.51) \text{ kJ}\cdot\text{mol}^{-1}$  than that consistent with the CODATA key value for  $\Delta_f H_m^\circ(\text{SnO, cr, 298.15 K})$  ( $\Delta_f G_m^\circ(\text{SnO, cr, 298.15 K}) = -(251.91 \pm 0.23) \text{ kJ}\cdot\text{mol}^{-1}$ ). Generally solubility data favour values indicative for more soluble *i.e.* less stable phases.

Figure VII-9: Solubility of SnO(cr) in 1.0515 m NaClO<sub>4</sub> solutions (○: experimental data of [1966MES/IRA]; solid line: linear fit of the experimental data fixed slope  $-2.00$ ; dash dotted line:  $\Delta_f G_m^{\circ}(\text{SnO, cr, 298.15 K}) = -253.116 \text{ kJ}\cdot\text{mol}^{-1}$  ([1941GAR/HEI], [1942GOR/LEI]); dotted line:  $\Delta_f G_m^{\circ}(\text{SnO, cr, 298.15 K}) = -253.938 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\Delta(\log_{10} {}^*K_{s0}^{\circ}) = 0.1$ ); dash dot line:  $\Delta_f G_m^{\circ}(\text{SnO, cr, 298.15 K}) = -255.080 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\Delta(\log_{10} {}^*K_{s0}^{\circ}) = -0.1$ ).



Unfortunately neither Mesmer and Irani [1966MES/IRA], nor Garrett and Heiks [1941GAR/HEI], nor Gorman and Leighton [1942GOR/LEI] characterised their solid phases by taking the respective X-ray powder diffraction patterns.

Blue-black tetragonal tin(II) oxide, which is the stable form at 25 °C [1961DON/MOS2], is easily formed if an excess of sodium hydroxide is added to a solution of tin(II) chloride [1967KWE/VRO]. As other tin(II) oxide or tin(II) hydroxide phases are less stable and more soluble than black tetragonal SnO, Mesmer and Irani [1966MES/IRA] very probably investigated this phase.

The value of  $S_m^{\circ}(\text{O}_2, \text{g}, 298.15 \text{ K})$  can be taken from the auxiliary data in Table IV-1. This review selected  $S_m^{\circ}(\text{SnO, cr}, 298.15 \text{ K}) = (57.18 \pm 0.22) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_m^{\circ}(\text{Sn, white}, 298.15 \text{ K}) = (51.18 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , thus  $\Delta_f S_m^{\circ}$  for Reaction (VII.22) can be calculated and  $\Delta_f G_m^{\circ}(\text{SnO, tetragonal}, 298.15 \text{ K})$  can be obtained from measured  $\Delta_f H_m^{\circ}$  or vice versa





$$\Delta_f S_m^\circ ((\text{VII.22}), 298.15 \text{ K}) = - (96.58 \pm 0.23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

As summarised in Table VII-3 the selection of  $\Delta_f G_m^\circ$  as well as  $\Delta_f H_m^\circ$  causes some problem.

Table VII-3: Values of the Gibbs energy and enthalpy of formation of SnO(cr).

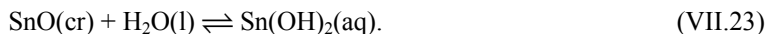
$\Delta_f H_m^\circ$ (SnO, cr, 298.15 K)/ kJ·mol <sup>-1</sup>	$\Delta_f G_m^\circ$ (SnO, cr, 298.15 K)/ kJ·mol <sup>-1</sup>	references
-280.71 ± 0.21*	-251.91 ± 0.22	[1981LAV/TIM]
-281.92 ± 1.38	-253.12 ± 1.38*	[1941GAR/HEI], [1942GOR/LEI]
-283.31 ± 0.57	-254.51 ± 0.57*	[1966MES/IRA]
-286.00 ± 1.34*	-257.20 ± 1.34	[1953HUM/OBR]
-286.03 ± 0.67	-257.23 ± 0.67* cell1	[1929MAI]
-282.46 ± 1.40	-253.66 ± 1.40* cell2	[1929MAI]

\* experimentally determined

The value of Lavut *et al.* had to be rejected, as the solubility data of [1941GAR/HEI], [1942GOR/LEI] and [1966MES/IRA], the combustion calorimetry data of [1953HUM/OBR] and the data from two different galvanic cell-potential measurements of [1929MAI] weighted by uncertainties result in the selected value:

$$\Delta_f H_m^\circ (\text{SnO, tetragonal, 298.15 K}) = - (284.24 \pm 0.76) \text{ kJ}\cdot\text{mol}^{-1}.$$

Garret and Heiks [1941GAR/HEI] determined the solubility of SnO(cr) in pure water under oxygen-free conditions according to reaction



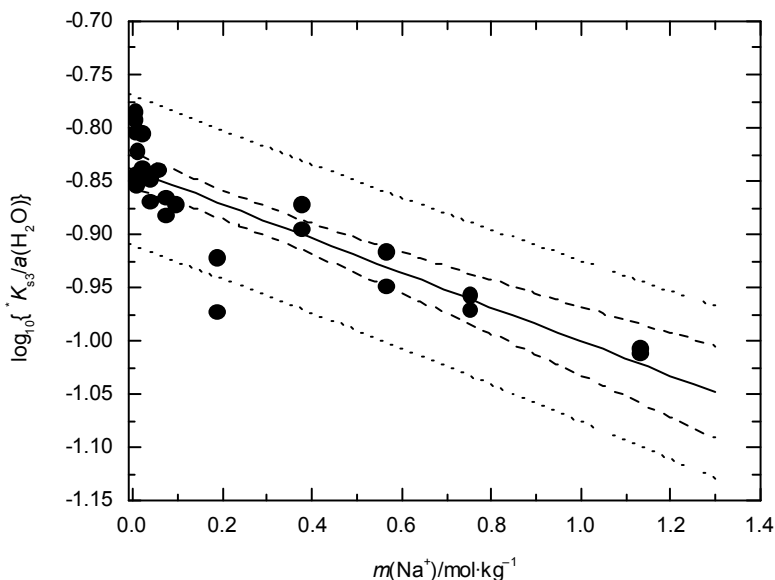
The accurate determination of the rather low Sn(II) molality ( $\approx 5 \times 10^{-6}$  mol·kg<sup>-1</sup>) at saturation is quite difficult, but there seems to be no other information available on Reaction (VII.23). Thus provisional values are listed for comparison:  $\log_{10} K_{s2}^\circ ((\text{VII.23}), 298.15 \text{ K}) = - (5.30 \pm 0.13)$  and  $\Delta_f G_m^\circ (\text{Sn}(\text{OH})_2, \text{aq}, 298.15 \text{ K}) = - (462.32 \pm 1.06) \text{ kJ}\cdot\text{mol}^{-1}$ .

Garret and Heiks [1941GAR/HEI] determined the solubility of tin(II) oxide in an alkaline medium according to Reaction (VII.24) by equilibrating SnO(s) with sodium hydroxide solutions at 25 °C.



The SIT analysis of these data resulted in  $\log_{10} {}^*K_{s3}^\circ ((\text{VII.24}), 298.15 \text{ K}) = - (0.84 \pm 0.02)$  and  $\varepsilon(\text{Na}^+, \text{Sn}(\text{OH})_3^-) = (0.12 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$  see Figure VII-10.

Figure VII-10: Solubility of SnO(cr) in NaOH solutions (●: experimental data [1941GAR/HEI]; solid line: linear fit; dashed lines: confidence limits; dotted lines: prediction limits).



A still older study on the solubility of “Sn(OH)<sub>2</sub>”(s) in sodium hydroxide solutions [1902RUB], where information concerning the equilibration temperature is lacking, resulted in a similar value of  $\log_{10} {}^*K_{s3}^{\circ} = -(0.86 \pm 0.04)$ .

With the NEA auxiliary data for  $\Delta_f G_m^{\circ}(\text{OH}^-, 298.15 \text{ K})$ ,  $\Delta_f G_m^{\circ}(\text{H}_2\text{O}, 1, 298.15 \text{ K})$  and  $\Delta_f G_m^{\circ}(\text{SnO}, \text{cr}, 298.15 \text{ K})$  selected by this review team,

$$\Delta_f G_m^{\circ}(\text{Sn(OH)}_3^-, 298.15 \text{ K}) = -(645.01 \pm 0.77) \text{ kJ}\cdot\text{mol}^{-1}$$

is obtained and has been selected, see Section VII.1.1.

#### VII.2.2.4 Selected data

The thermodynamic data from previous critical evaluations are summarised in Table VII-4.

The choice of the value of enthalpy of formation of SnO(cr) is difficult based on the data listed above and must be made on the basis of additional constraints as reviewed in Section VII.2.2.3. As discussed in Appendix A, the critique of Humphrey and O'Brien [1953HUM/OBR] data by Lavut *et al.* [1981LAV/TIM] is not totally justified. Since the solubility data discussed in Section VII.2.2.3 favour the lower value

of the enthalpy, we have taken the average of the enthalpy data from the five low values [1966MES/IRA], [1953HUM/OBR], [1942GOR/LEI], [1941GAR/HEI] and [1929MAI], see Table VII-3.

Table VII-4: Previous critical evaluations of the thermodynamic data for SnO(cr).

$\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C_{p,m}^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Reference
$-280.71 \pm 0.20$	$57.17 \pm 0.30$	$47.78 \pm 0.30$	CODATA
$-280.68 \pm 0.17$	$57.167 \pm 0.291$		[1987LAM/HIL]
$-280.71 \pm 0.21$			[1991GUR/VEY]

The selected heat capacity and entropy given below are based on Eq. (VII.15) and the linear regression of  $T$ ,  $C_{p,m}^\circ$  data between  $263 \leq T/\text{K} \leq 311$ , see Appendix A entry on [1978KOS/SAM], respectively.

$$S_m^\circ (\text{SnO, cr, 298.15 K}) = (57.18 \pm 0.22) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1},$$

$$C_{p,m}^\circ (\text{SnO, cr, 298.15 K}) = (47.76 \pm 0.08) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

Analysis of the solubility data (see Table VII-3, Section VII.2.2.3) clearly establishes that the following value of enthalpy should be selected:

$$\Delta_f H_m^\circ (\text{SnO, cr, 298.15 K}) = -(284.24 \pm 0.76) \text{ kJ}\cdot\text{mol}^{-1}.$$

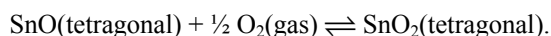
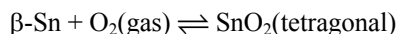
This selection yields:

$$\Delta_f G_m^\circ (\text{SnO, cr, 298.15 K}) = -(255.44 \pm 0.76) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VII.2.3 SnO<sub>2</sub>(cr)

### VII.2.3.1 Enthalpy of formation of SnO<sub>2</sub>(cr)

Lavut *et al.* [1981LAV/TIM] determined the enthalpy of formation of oxides using a combustion calorimeter. The enthalpies of formation of the oxides were calculated from the reactions:



The value of the standard enthalpy of formation of SnO<sub>2</sub>(tetragonal), is

$$\Delta_f H_m^\circ (\text{SnO}_2, \text{tetragonal, 298.15 K}) = -(577.63 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}.$$

There are several determinations of the standard Gibbs energy of formation of SnO<sub>2</sub>(tetragonal) over the temperature range 673 to 1373 K using electrochemical

techniques (see Table A-30). Seetharaman and Staffansson [1977SEE/STA] determined the equation for the standard Gibbs energy of formation of SnO<sub>2</sub>(tetragonal) as:

$$[\Delta_f G_m^\circ]_{990\text{K}}^{1373\text{K}}(\text{SnO}_2, \text{tetragonal}, T) = - [575.066 - 0.207376 (T/\text{K})] \pm 0.920 \text{ kJ}\cdot\text{mol}^{-1}.$$

These data were shown to be closely consistent with a number of other studies. For the calculation of the standard state quantities, these data cannot be used but it may be possible to check the consistency of the finally selected values at 298 K with a heat-capacity equation with the several data based on the cell-potential measurements (*e.g.* Petot-Ervos *et al.* [1975PET/FAR]). Gorbachev and Nekrasov [1976GOR/NEK] made an assessment of the Gibbs energy of formation of SnO<sub>2</sub>(tetragonal) in the system with Cu-Fe-Sn-S-H<sub>2</sub>O. These are phase equilibrium experiments and cannot be used here except again for checking the consistency with our finally selected data. As an example,  $\Delta_f G_m^\circ(\text{SnO}_2, \text{tetragonal}, 673 \text{ K}) = -(438.19 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$ .

The values recommended by Lamoreaux and Hildenbrand [1987LAM/HIL] for  $\Delta_f H_m^\circ(\text{SnO}_2, \text{tetragonal}, 298.15 \text{ K})$  and  $S_m^\circ(\text{SnO}_2, \text{tetragonal}, 298.15 \text{ K})$  are  $-(577.574 \pm 0.166) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(49.011 \pm 0.081) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  respectively.

Mallika *et al.* [2001MAL/EDW] showed that SnO(cr) disproportionated into Sn(l) and SnO<sub>2</sub>(cr) at 800 K at a controlled rate of heating. They measured the potential of a galvanic cell with SnO/SnO<sub>2</sub> as the test electrode and ( $p_{\text{O}_2} \approx 10^{-3} \text{ atm}$ )Pt or Fe|Fe<sub>x</sub>O as the reference electrodes using  $x_{\text{YO}_{1.5}} = 0.15$  of YSZ (yttria stabilised zirconia) as the electrolyte over a temperature range from 772 to 1206 K. The data yielded the following expression for the Gibbs energy of formation of SnO<sub>2</sub> as:  $\Delta_f G_m^\circ(\text{SnO}_2, \text{tetragonal}, T) = -(568.9 - 0.2007 T/\text{K}) \text{ kJ}\cdot\text{mol}^{-1}$ . To calculate the enthalpy of formation, Mallika *et al.* performed a third-law analysis of the 60 data points making use of the free energy functions for SnO<sub>2</sub> and the elements compiled by Lamoreaux *et al.* [1987LAM/HIL]. Their calculated value is  $\Delta_f H_m^\circ(\text{SnO}_2, \text{tetragonal}, 298.15 \text{ K}) = -(578.3 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$ .

### VII.2.3.2 Heat capacity of SnO<sub>2</sub>(cr)

There are a number of studies on the heat capacity of SnO<sub>2</sub>(cr), cassiterite, with the latest study of Gurevich *et al.* [2004GUR/GAV2] and [2004GUR/GAV3]. Zhogin *et al.* [1980ZHO/KOS] measured the heat capacity of crystalline tin dioxide in a vacuum adiabatic calorimeter. Thermodynamic functions  $(H_T - H_{0\text{K}})/T$ ,  $(S_T - S_{0\text{K}})$ ,  $-(G_T - G_{0\text{K}})/T$  were calculated based on heat capacity of SnO<sub>2</sub>(cass) measured at 58 points in the temperature range 10 to 300 K. No anomalies on the heat-capacity curve were observed. Deviations of experimental points from smooth curve are: 20% in the 10 to 17 K range, less than 10% in the 17 to 30 K range, less than 3% in the 30 to 100 K range, less than 0.3% in the 100 to 200 K range and less than 0.2% in the 200 to 300 K range. Equation  $C_{p,m}^\circ(\text{SnO}_2, \text{cass}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 2.51 \times 10^{-5} \times (T/\text{K})^3$  was used to extrapolate  $C_{p,m}^\circ(\text{SnO}_2, \text{cass}, T)$  to 0 K. The data of this study are given in Appendix A (Table A-70).

Gurevich *et al.* [2004GUR/GAV2] and [2004GUR/GAV3] measured the heat capacity of SnO<sub>2</sub>(cass) in the temperature range of 13.4 to 336 K using an adiabatic calorimeter. Two samples of tin dioxide with  $w(\text{SnO}_2) = 99.906\%$  (RP) and  $w(\text{SnO}_2) = 99.996\%$  (AA), respectively, were investigated, see Table A-70. They used the Debye-Einstein-Kieffer equation to fit their experimental data (see Eq. (A.85)). The resulting data on heat capacity and entropy are displayed in Table VII-5 and compared with a conventional fitting equation which was conducted as follows.

Table VII-5: Comparison of thermodynamic data of SnO<sub>2</sub> (tetragonal) at 298.15 K.

	[2004GUR/GAV2]	this review
$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$55.24 \pm 0.03$	$55.26 \pm 0.09$
$S_m^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$51.82 \pm 0.07$	$51.77 \pm 0.14$
$[H_m^{\circ}(T) - H_m^{\circ}(0\text{K})] / \text{kJ}\cdot\text{mol}^{-1}$	$8.806 \pm 0.005$	$8.805 \pm 0.017$

The first step was to examine up to which temperature the heat capacity of SnO<sub>2</sub>(cr) obeys Debye's  $T^3$  law, see Figure VII-11. In fact the first 17  $C_{p,m}^{\circ}$  values of [1980ZHO/KOS] and [2004GUR/GAV3] are within the experimental uncertainty proportional to  $T^3$  and at 16 K the heat capacity ( $C_{p,m}^{\circ}(\text{SnO}_2 \text{ cr}, 16 \text{ K}) = 0.168 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) agrees closely with that derived by Gurevich *et al.* From  $T_0 = 16 \text{ K}$  to 336 K,  $C_{p,m}^{\circ}(T)$  was approximated by Eq. (VII.25) containing 6 adjustable parameters ( $a$  to  $f$ ) whose numerical values refer to  $C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $T/\text{K}$ , see also Table A-73.

$$\begin{aligned}
 [C_{p,m}^{\circ}(T) - C_{p,m}^{\circ}(T_0)] / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = & a [(T - T_0)/\text{K}] + b [(T/\text{K})^2 - (T_0/\text{K})^2] \\
 & + c [(T/\text{K})^{-2} - (T_0/\text{K})^{-2}] + d [(T/\text{K})^{-3} - (T_0/\text{K})^{-3}] \\
 & + e [(T/\text{K})^{-0.5} - (T_0/\text{K})^{-0.5}] + f [(T/\text{K})^{-1} - (T_0/\text{K})^{-1}]
 \end{aligned}
 \tag{VII.25}$$

	$a$	$b$	$c$	$d$	$e$	$f$
Eq. (VII.25)	$1.7419 \times 10^{-1}$	$-2.1858 \times 10^{-4}$	$-2.9144 \times 10^4$	$1.1389 \times 10^5$	$-1.0659 \times 10^3$	$4.4830 \times 10^3$

The uncertainty of  $C_{p,m}^{\circ}(T)$  was estimated by

$$s(C_{p,m}^{\circ}) = \sqrt{\frac{\sum_{i=1}^N \{C_{p,m}^{\circ}(\text{obsd}) - C_{p,m}^{\circ}(\text{calc})\}^2}{N - 7}} = 0.089 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Thermodynamic functions

$$S_m^{\circ}(T) = \int_{0\text{K}}^T (C_{p,m}^{\circ}/T) dT$$

and

$$H_m^{\circ}(T) - H_m^{\circ}(0\text{K}) = \int_{0\text{K}}^T C_{p,m}^{\circ} dT$$

have been calculated using Eq. (VII.25). In order to obtain consistent uncertainties two  $T$ ,  $C_{p,m}^{\circ}$  data sets were prepared by adding and subtracting the expression

$$\sqrt{\{C_{p,m}^{\circ}(\text{obsd}) - C_{p,m}^{\circ}(\text{calc})\}^2}$$

from individual  $C_{p,m}^{\circ}$  values. These sets of  $C_{p,m}^{\circ}$  values were approximated by Eq. (VII.25) again. Integrating of thus modified  $C_{p,m}^{\circ}$  functions resulted in lower and upper  $S_m^{\circ}(T)$  and  $H_m^{\circ}(T) - H_m^{\circ}(0\text{K})$  values, respectively. The uncertainties of  $S_m^{\circ}(298.15\text{ K})$  and  $H_m^{\circ}(298.15\text{ K}) - H_m^{\circ}(0\text{K})$  were estimated by dividing the difference of the lower and upper values by two.

Figure VII-11:  $C_{p,m}^{\circ}$  ( $\text{SnO}_2$ , cass), extrapolation to  $T \rightarrow 0$ .

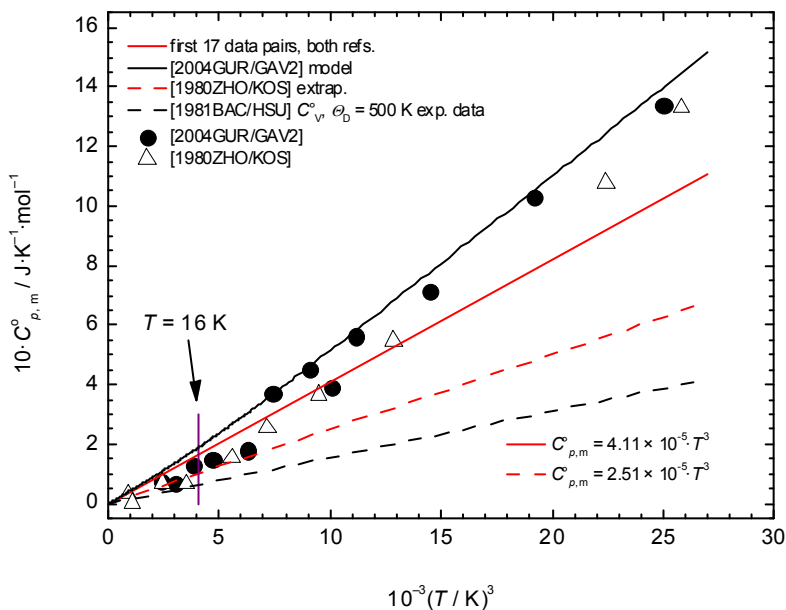
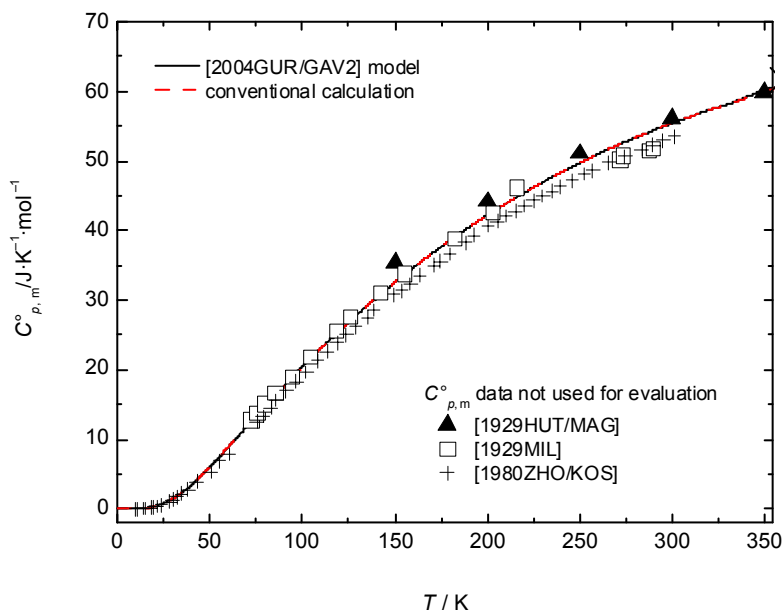


Table VII-5 shows that conventionally obtained values of  $C_{p,m}^{\circ}(298.15\text{ K})$ ,  $S_m^{\circ}(298.15\text{ K})$  and  $H_m^{\circ}(298.15\text{ K}) - H_m^{\circ}(0\text{K})$  agree with those obtained by Gurevich *et al.*'s model within the range of uncertainties given by [2004GUR/GAV2] and [2004GUR/GAV3]. The uncertainties estimated by the method outlined above are somewhat more pessimistic than those of Gurevich *et al.*

The low temperature (0 – 336 K) values of heat capacity, entropy and enthalpy increment calculated on the basis of Eqs. (A.82), (A.83) and (A.84) are compared with the values calculated by a conventional procedure, see Table A-65. Figure VII-12 shows that low-temperature heat capacities of tin dioxide calculated by Gurevich *et al.*'s model essentially coincide with those obtained by the conventional procedure used.

Figure VII-12: Low-temperature heat capacity of SnO<sub>2</sub>(cass).



Gurvich *et al.* [2004GUR/GAV] also reviewed two other sets of data [1929HUT/MAG], [1929MIL2] in the temperature range of interest (below 300 K) showing disparate values. A summary of the key values on the thermodynamic data of SnO<sub>2</sub>(cr) is given in Table VII-6.

The two major sets of data, [1980ZHO/KOS] and [2004GUR/GAV3], differ significantly from each other. Gurevich *et al.* [2004GUR/GAV2] list three reasons why they believe that their data are more reliable than those of [1980ZHO/KOS]. (1) The calorimetric unit was tested using the standard sample directly before the measurements, (2) the data obtained for two samples are in good agreement with each other and with data from [1936KAP/ZIL] within the high-temperature interval, and (3) sample AA was prepared using the same procedure as by [1980ZHO/KOS].

Table VII-6: Key values of the thermodynamic data of cassiterite at 298 K.

$\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$S_m^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$C_{p,m}^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Method	Reference
$-577.63 \pm 0.20$	$49.04 \pm 0.10$		critical evaluation	CODATA
$-577.574 \pm 0.166$	$49.011 \pm 0.081$		critical evaluation	[1987LAM/HIL]
$-578.0 \pm 1.4$			galvanic cell potential/ calculated	[1986BAN]
$-577.63 \pm 0.16$			calorimetry	[1981LAV/TIM]
	$49.01 \pm 0.10$	$53.22 \pm 0.11$	calorimetry	[1980ZHO/KOS]
$-578.3 \pm 4.0$			galvanic cell potential/ calculated	[2001MAL/EDW]
$-577.8 \pm 1.0$			galvanic cell potential/third law	[1977SEE/STA]
	$51.82 \pm 0.07$	$55.28 \pm 0.03$	calorimetry	[2004GUR/GAV]

When the heat capacities measured by [2004GUR/GAV3], [1980ZHO/KOS], [1929MIL], and [1929HUT/MAG] are approximated by Eq. (A.85) the estimated uncertainty increases by one order of magnitude

$$S(C_{p,m}^\circ) = \sqrt{\frac{\sum_1^N \{C_{p,m}^\circ(\text{obsd}) - C_{p,m}^\circ(\text{calc})\}^2}{N-7}} = 0.81 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

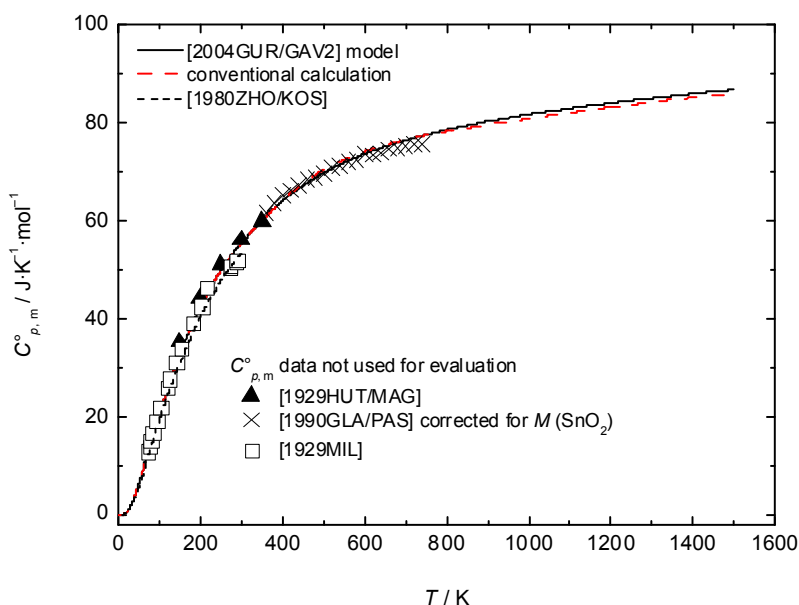
and a mean value of  $C_{p,m}^\circ(\text{SnO}_2, \text{tetragonal}, 298.15 \text{ K}) = (54.82 \pm 0.81) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is obtained. While this value overlaps with the value recommended by [2004GUR/GAV] it is significantly higher than  $C_{p,m}^\circ(\text{SnO}_2, \text{tetragonal}, 298.15 \text{ K}) = (53.22 \pm 0.11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  given by [1980ZHO/KOS]. Consequently the data selected in this review are based on the experimental results of [2004GUR/GAV2] and [2004GUR/GAV3]. It should, however, be emphasised that the uncertainties given in [2004GUR/GAV] are too optimistic.

Figure VII-13 shows the heat-capacity function of tin dioxide in the whole temperature range investigated so far. A minor difference between conventional evaluation and Gurevich *et al.*'s model becomes visible at  $T > 800 \text{ K}$ .

Glazov *et al.* [1990GLA/PAS] used an erroneous molar mass for  $\text{SnO}_2$  ( $M_{\text{SnO}_2} = 143.69 \text{ g}\cdot\text{mol}^{-1}$  instead of  $150.7088 \text{ g}\cdot\text{mol}^{-1}$ ) in their calculation. After correction their data agree reasonably with the curves based on the results of [2004GUR/GAV2].

The reviewer concluded that the  $C_{p,m}^\circ(\text{SnO}_2, T)$  data of Gurevich *et al.* provide the most reliable basis for  $S_m^\circ(T)$  and  $H_m^\circ(T) - H_m^\circ(0 \text{ K})$  of tin dioxide, cassiterite.



Figure VII-13: Heat capacity of SnO<sub>2</sub>(cass).

Based on the review of all data, the following values are selected:

$$\Delta_f H_m^\circ(\text{SnO}_2, \text{cass}, 298.15 \text{ K}) = -(577.63 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1},$$

$$S_m^\circ(\text{SnO}_2, \text{cass}, 298.15 \text{ K}) = (51.77 \pm 0.14) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$C_{p,m}^\circ(\text{SnO}_2, \text{cass}, 298.15 \text{ K}) = (55.26 \pm 0.09) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^\circ(\text{SnO}_2, \text{cass}, 298.15 \text{ K}) = -(516.64 \pm 0.21) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

It is possible to combine the high temperature data of Kapustinskii *et al.* [1936KAP/ZIL] and the data of Gurevich *et al.* [2004GUR/GAV2] in the temperature range from 296.90 to 336.88 K with Eq. (VII.25). According to Kapustinskii *et al.* [1936KAP/ZIL] their  $C_{p,m}^\circ(T)$  function is given by the following Maier and Kelley equation [1932MAI/KEL]

$$C_{p,m}^\circ(T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/\text{K} + c (T/\text{K})^{-2}. \quad (\text{VII.26})$$

Equation (VII.26) was used to calculate  $C_{p,m}^\circ(T)$  in the range from 595 to 1496 K. Coefficients of the equations are listed in Table A-73 and the data are tabulated in Table A-74.

## VII.3 Gaseous tin hydrides

### VII.3.1 SnH<sub>4</sub>(g)

Tin tetrahydride, or stannane SnH<sub>4</sub>, is a gas under ambient conditions; the normal boiling point is 221.4 K [1952ROS/WAG]. Experimental data to 1964 for formation properties of stannane were reviewed by [1964JEF/MCK].

The ideal gas heat capacity of stannane may be deduced from spectroscopic data. Such data are given in [1961MAY/DIL], [1965LEV/ZIF], [1966WIL/WIL] and [1964DEV/YUS]. The model chosen for calculations is generally the harmonic oscillator-rigid rotator approximation. The results of original calculations and compilations/ evaluations are given in Table VII-7. The compilations [1952ROS/WAG] and [1982WAG/EVA] both give a value (at 298 K only) of 48.95 J·K<sup>-1</sup>·mol<sup>-1</sup> without discussion or stating source. The tabulated data of [1977BAR/KNA] and [1993BAR] were taken from [1962GLU] and/or [1970GLU] (the exact source is not clear). The only fitting equation available was given by [1977BAR/KNA]:

$$C_{p,m}^{\circ}(\text{SnH}_4, \text{g}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 51.80 + 0.03766 T/\text{K} - 1.130 \times 10^6 (T/\text{K})^{-2} \quad (\text{VII.27})$$

and no uncertainty was given. Values from this equation are included in Table VII-7.

Table VII-7: The heat capacity of stannane ideal gas from spectroscopic data <sup>(a)</sup>.

T/K	C <sub>p,m</sub> <sup>o</sup> (SnH <sub>4</sub> , g, T)/J·K <sup>-1</sup> ·mol <sup>-1</sup>				
	Original calculations		Compilations		Tabulated
	[1961MAY/DIL]	[1969SHA/MOR]	[1993BAR]	[1977BAR/KNA]	Eq. (VII.27)
221	41.1				
273	46.48				46.92
298.15	49.08	50.59	50.585	50.317	50.32
300		50.75	50.810	50.543	50.88
373	56.90				57.73
400		59.79	60.068	59.798	59.80
423	60.42				61.41
500		67.24	66.375		66.11
600		73.51	71.521	71.254	71.26

(a) The number of significant figures shown are those of the experimenter/evaluator.

The standard entropy of the ideal gas was calculated from molecular constants. The results of original calculations and values from compilations are given in Table VII-8. The tabulated data of [1977BAR/KNA] and [1993BAR] were taken from

[1962GLU] and/or [1970GLU]. The value of [1964JEF/MCK] was estimated by analogy with other hydrides of Group 14.

Table VII-8: Standard entropy of stannane.

Reference	Type of data source	$S_m^0$ (SnH <sub>4</sub> , g, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	Uncertainty
[1952ROS/WAG]	Compilation	227.6	
[1964JEF/MCK]	Compilation	226	± 2 (original)
[1969SHA/MOR]	Experimental	228.7	
[1973SHI/MAR]	Experimental	228.3	
[1977BAR/KNA]	Compilation	228.7	
[1982WAG/EVA]	Compilation	227.68	
[1993BAR]	Compilation	228.765	

For the enthalpy of formation Gunn and Green [1961GUN/GRE] derived a value of 162.8 kJ·mol<sup>-1</sup> from heats of explosive decomposition. Saalfeld and Svec [1961SAA/SVE] used mass spectrometry (96.2 kJ·mol<sup>-1</sup>). Published data are given in Table VII-9.

Table VII-9: Standard enthalpy of formation of stannane.

Reference	Type of data source	$\Delta_f H_m^0$ (SnH <sub>4</sub> , g, 298.15 K)/ kJ·mol <sup>-1</sup>	Uncertainty
[1952ROS/WAG]	Compilation	163	
[1961GUN/GRE]	Experiment	162.8	± 2.1 (original)
[1961SAA/SVE]	Experiment	96.2	
[1969SHA/MOR]	Calculation	166	
[1977BAR/KNA]	Compilation	163	
[1982WAG/EVA]	Compilation	162.8	
[1993BAR]	Compilation	162.8	

No data source suggests an uncertainty in  $C_{p,m}^0$ , but the reviewer assigned a value of ± 3.0 J·K<sup>-1</sup>·mol<sup>-1</sup>. With the use of Eq. (VII.27) and data in Table VII-7, the selected data are generated by the equation

$$[C_{p,m}^0]_{298K}^{600K}(\text{SnH}_4, \text{g}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 51.80 + 0.03766 T/\text{K} - 1.130 \times 10^6 (T/\text{K})^{-2}.$$

The selected value for the standard entropy, from Table VII-8, is:

$$S_m^\circ(\text{SnH}_4, \text{g}, 298.15 \text{ K}) = (227.8 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The uncertainty has been assigned by this review.

The selected value of the standard enthalpy of formation of stannane, from Table VII-9, is:

$$\Delta_f H_m^\circ(\text{SnH}_4, \text{g}, 298.15 \text{ K}) = (162.8 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^\circ(\text{SnH}_4, \text{g}, 298.15 \text{ K}) = (188.1 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

# Chapter VIII

## Group 17 (halogen) compounds and complexes

### VIII.1 Halide compounds

#### VIII.1.1 Solid fluorides

Tin(II) fluoride ( $\text{SnF}_2$ ) is a white crystalline solid with a melting point of  $(486 \pm 2)$  K [1991GUR/VEY] and a boiling point of 1123 K.

There are three forms ( $\alpha$  = monoclinic,  $\beta$  = orthorhombic,  $\gamma$  = tetragonal) known. The usual form at room temperature is monoclinic. From concentrated aqueous solutions beside the monoclinic also an orthorhombic form can be crystallised [1965DON/OTE] (named  $\alpha$  form by these authors).  $\alpha$ - $\text{SnF}_2$  undergoes a sluggish first order transition to  $\gamma$ - $\text{SnF}_2$  at  $150 - 180$  °C [1981DEN]. The latter transforms in a second order transition below  $66$  °C to  $\beta$ - $\text{SnF}_2$  [1980DEN/PAN].  $\beta$ - $\text{SnF}_2$  is metastable at any temperature [1981DEN].

Tin(IV) fluoride ( $\text{SnF}_4$ ) is a white crystalline solid (space group  $I4/mmm$ ) [1996BOR/HOP]; its melting point has not been determined exactly, in [1972GME]  $T_{\text{fus}} = 715$  K is given. Its boiling point at 978 K [1904RUF/PLA] was identified later as sublimation temperature at ambient pressure [1956WOO].

Crystalline compounds between tin(II) and tin(IV) fluoride with composition  $\text{Sn}_2\text{F}_6$  [1990RUC/MIR] and  $\text{Sn}_3\text{F}_8$  ([1973DOV/KIN], [1979FRL/GAN], [1992TOM]) are known and characterised structurally, but no thermodynamic data have been measured.

##### VIII.1.1.1 $\text{SnF}_2(\text{cr})$

The enthalpies of reactions of  $\text{SnO}(\text{cr})$  and  $\text{SnF}_2(\text{cr})$  with hydrofluoric acid were measured in an isothermic-shell calorimeter by Solov'ev *et al.* [2001SOL/VLA]. The results were used together with the literature data to calculate the standard enthalpy of formation of  $\text{SnF}_2(\text{cr})$  at 298.15 K ( $\Delta_f H_m^\circ(\text{SnF}_2, \text{cr}, 298.15 \text{ K}) = -(695.2 \pm 1.7)$  kJ·mol<sup>-1</sup>). The thermochemical cycle used for determination of enthalpy of  $\text{SnF}_2(\text{cr})$  involved several reactions, as shown in Table VIII-1.

Originally, the data for SnO(cr) were the calorimetric data measured by Lavut *et al.* [1981LAV/TIM]. However as reviewed in Section VII.2.2.3, the enthalpy of formation of SnO is chosen to be  $-(284.24 \pm 0.76)$  kJ·mol<sup>-1</sup>. The enthalpy of formation of HF(aq) has been taken from the selected auxiliary data (Table IV-1). Therefore, the value

$$\Delta_f H_m^\circ (\text{SnF}_2, \text{cr}, 298.15 \text{ K}) = -(699.9 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

is selected. This value differs vastly from the calculated/estimated value of  $-(677 \pm 10)$  kJ·mol<sup>-1</sup> by Gurvich and Veyts [1991GUR/VEY].

Table VIII-1: Thermochemical cycle used in [2001SOL/VLA].

Reaction	$-\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	Reference
1 SnF <sub>2</sub> (cr) + HF(aq) ⇌ H[SnF <sub>3</sub> ](aq)	12.00 ± 0.30	
2 SnO(cr) + 3 HF(aq) ⇌ H[SnF <sub>3</sub> ](aq) + H <sub>2</sub> O(l)	67.20 ± 1.40	
3 H <sub>2</sub> (g) + ½ O <sub>2</sub> (g) ⇌ H <sub>2</sub> O(l)	285.83 ± 0.05	[1982GLU], [1989COX/WAG]
4 ½ H <sub>2</sub> (g) + ½ F <sub>2</sub> (g) ⇌ HF(aq)	323.15 ± 0.72	NEA TDB auxiliary data
5 Sn(cr) + ½ O <sub>2</sub> (g) ⇌ SnO(cr)	284.24 ± 0.76	This review
6 Sn(cr) + F <sub>2</sub> (g) ⇌ SnF <sub>2</sub> (cr)	699.91 ± 2.17	

$$\Delta_f H (\text{SnF}_2, \text{cr}) = \Delta_f H_6 = -\Delta_f H_1 + \Delta_f H_2 - \Delta_f H_3 + 2\Delta_f H_4 + \Delta_f H_5$$

Thourey *et al.* [1983THO/PER] determined the standard enthalpies of formation of SnF<sub>2</sub>(cr), PbF<sub>2</sub>(cr) and PbSnF<sub>4</sub>(cr) by alkaline hydrolysis and obtained a value of  $-(736 \pm 16)$  kJ·mol<sup>-1</sup> for the enthalpy of formation of SnF<sub>2</sub>(cr). The error is unacceptably high.

There are no other thermochemical data on this system. However, from solubility studies in the system SnF<sub>2</sub>-HF-H<sub>2</sub>O,  $\Delta_f G_m^\circ (\text{SnF}_2, \text{cr}, 298.15 \text{ K}) = -(639 \pm 1)$  kJ·mol<sup>-1</sup> was estimated (see Section VIII.2.1.1).

### VIII.1.1.2 Ternary fluorides

#### VIII.1.1.2.1 PbSnF<sub>4</sub>(cr)

The heat capacity was measured by adiabatic calorimetry at 10 to 352 K [1988CAL/WEI] and by DSC at 270 to 650 K [1991CAL/WEI]. A number of previous investigations [1978REA/LUC], [1979PAN/DEN], [1980PER/VIL] and [1981CLA/LET] used DTA, DSC, XRD and dilatometry and claimed solid-solid transitions at 353 (350), 533, 628 (623, 620) and 653 K. In some cases enthalpies of transition and lattice parameters were reported. The heat-capacity measurements of [1991CAL/WEI] are here taken as definitive, and were interpreted [1991CAL/WEI] as establishing the following transitions as veridical:

$\alpha$  (monoclinic)  $\rightarrow$   $\beta$  (tetragonal), 353 K,  $\Delta_{\text{trs}}H = (306.0 \pm 0.2) \text{ J}\cdot\text{mol}^{-1}$ ,

$\beta$  (tetragonal)  $\rightarrow$   $\gamma$  (cubic), 600 K,  $\Delta_{\text{trs}}H = (2.53 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ .

Uncertainties, unless otherwise stated, are those of the experimenter.

The melting point was reported as 666 K [1981CLA/LET]. The heat-capacity data were fitted to the equations:

$$[C_{p,m}^{\circ}]_{270\text{K}}^{353\text{K}}(\text{PbSnF}_4, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -235.11 + 2.42159 T/\text{K} - 0.00365 (T/\text{K})^2$$

with standard error of estimate =  $0.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , leading to

$$C_{p,m}^{\circ}(\text{PbSnF}_4, \alpha, 298.15 \text{ K}) = (162.4 \pm 0.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

and

$$[C_{p,m}^{\circ}]_{353\text{K}}^{600\text{K}}(\text{PbSnF}_4, \beta, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -333.279 + 4.15949 T/\text{K} \\ - 0.01166 (T/\text{K})^2 + 1.09843 \times 10^{-5} (T/\text{K})^3$$

with standard error of estimate =  $5.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , which are selected here.

From the heat-capacity measurements up to 298 K [1988CAL/WEI], the selected entropy is:

$$S_{\text{m}}^{\circ}(\text{PbSnF}_4, \text{cr}, 298.15 \text{ K}) = (223.7 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The enthalpy of formation was measured by alkaline hydrolysis calorimetry by [1983THO/PER] who reported:  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PbSnF}_4, \text{cr}, 298.15 \text{ K}) = -(1371.4 \pm 31.8) \text{ kJ}\cdot\text{mol}^{-1}$ . As this datum has not been confirmed by independent measurements, it cannot be selected by this review.

#### VIII.1.1.2.2 BaSnF<sub>4</sub>(cr)

This compound decomposes above 673 K before melting [1975DEN/PAN]. The heat capacity was measured at 7 to 345 K by adiabatic calorimetry [1988CAL/WEI2] and at 310 to 650 K by DSC [1991CAL/WEI]. Combined data in the range 290 to 600 K were fitted by the following equation

$$[C_{p,m}^{\circ}]_{290\text{K}}^{600\text{K}}(\text{BaSnF}_4, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -9.43794 + 1.03157 T/\text{K} - 0.00219 (T/\text{K})^2 \\ + 1.62305 \times 10^{-6} (T/\text{K})^3$$

with standard error of estimate of  $0.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , leading to the selected value

$$C_{p,m}^{\circ}(\text{BaSnF}_4, \text{cr}, 298.15 \text{ K}) = (146.5 \pm 1.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

From heat-capacity data up to 298 K, the selected entropy is [1988CAL/WEI2]

$$S_{\text{m}}^{\circ}(\text{BaSnF}_4, \text{cr}, 298.15 \text{ K}) = (205.1 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

There is no reported value of standard enthalpy of formation for this compound.

### VIII.1.1.2.3 SrSnF<sub>4</sub>(cr)

The heat capacity was measured by adiabatic calorimetry at 6 to 394 K [1989CAL/SHA] and by DSC at 340 to 600 K [1991CAL/WEI]. The data were fitted to the equation

$$[C_{p,m}^{\circ}]_{290\text{K}}^{600\text{K}}(\text{SrSnF}_4, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -172.407 + 2.29374 T/\text{K} - 0.00549 (T/\text{K})^2 + 4.67657 \times 10^{-6} (T/\text{K})^3.$$

The standard error of estimate is 3.8 J·K<sup>-1</sup>·mol<sup>-1</sup>. The selected value is:

$$C_{p,m}^{\circ}(\text{SnF}_4, \text{cr}, 298.15 \text{ K}) = (147.4 \pm 7.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

From the heat-capacity data up to 298 K, the selected entropy is [1989CAL/SHA]

$$S_{\text{m}}^{\circ}(\text{SrSnF}_4, \text{cr}, 298.15 \text{ K}) = (187.2 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

There is no reported value of standard enthalpy of formation for this compound.

## VIII.1.2 Solid chlorides

SnCl<sub>2</sub>(cr) is a white crystalline solid with a melting point of 520 K and a boiling point of 896 K.

Tin(IV) chloride SnCl<sub>4</sub> is a colorless liquid and will be treated in Section VIII.2.2.3.

### VIII.1.2.1 SnCl<sub>2</sub>(cr)

There is a limited number of calorimetric measurements on the enthalpy of formation of SnCl<sub>2</sub>(cr) [1882THO], [1941KAP], [1973VAS/VAS2] with a large spread in the results (−327 to −353 kJ·mol<sup>-1</sup>). The range, however, narrows to within 5 kJ·mol<sup>-1</sup> if we reject the results from [1941KAP] being too disparate from any other. Vasil'ev *et al.* [1973VAS/VAS2] determined the heats of solution of SnCl<sub>2</sub> in hydrochloric acid solutions containing hydrogen peroxide. The method of synthesis of the samples assures the purity and the reliability of the data. The authors used 1 M and 2 M HCl solutions at *w* = 1.5 and 2.5% H<sub>2</sub>O<sub>2</sub>, and the heats of dissolution were closely similar. Their results are reported in Table VIII-2. The weighted average of value and uncertainty are given as  $-(327.86 \pm 1.08) \text{ kJ}\cdot\text{mol}^{-1}$  in agreement with the value reported by [1973VAS/VAS2]  $-(78.36 \pm 0.26) \text{ kcal}\cdot\text{mol}^{-1}$ .

The enthalpy was also determined from potential measurements by Bugden and Shelton [1970BUG/SHE] who used displacement cells of the type:





For the reaction:  $\text{Sn}(\text{cr}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{SnCl}_2(\text{cr})$ , they obtained the following equations for the standard Gibbs energy of formation with the lead chloride ( $\text{PbCl}_2|\text{Pb}$ ) and silver chloride ( $\text{AgCl}|\text{Ag}$ ) electrodes respectively:  $\Delta_f G_m^\circ(T)/\text{kJ}\cdot\text{mol}^{-1} = -333.51 + 13170 T/\text{K}$  and  $\Delta_f G_m^\circ(T)/\text{kJ}\cdot\text{mol}^{-1} = -332.628 + 130440 T/\text{K}$ . No errors have been given. From these data, Bugden and Shelton proceeded to calculate the second and third law values of enthalpy at 298.15 K. In the third law calculation, they used an estimated value of the entropy of  $\text{SnCl}_2(\text{cr})$  ( $129.7 \pm 8.2$ )  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Their estimated data are:  $\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = -(338.1 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$  and  $S_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = (125.9 \pm 5.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , the latter values were both not considered in this review, details of the argument are given in the Appendix A entry for [1970BUG/SHE].

Table VIII-2: Enthalpies of formation of  $\text{SnCl}_2(\text{cr})$  as determined by Vasil'ev *et al.* [1973VAS/VAS2]. The data in the third and fourth columns correspond to two differently prepared samples. The weighted average value and its uncertainty are  $-(327.86 \pm 1.08) \text{ kJ}\cdot\text{mol}^{-1}$ .

$\text{H}_2\text{O}_2$ (%)	[HCl]/M	$\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$
1.5	1.0	$-328.57 \pm 2.64$	$-328.03 \pm 2.76$
	2.0	$-327.48 \pm 3.43$	$-326.35 \pm 3.64$
2.5	1.0	$-328.82 \pm 2.05$	
	2.0	$-326.77 \pm 2.30$	

Gurvich and Veyts [1991GUR/VEY] averaged the cell potential data and the calorimetric data and arrived at:  $\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = -(333 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$ . This is a big compromise which does not take into account that the averaged value based on electrochemical measurements,  $-(338.0 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$  [1970BUG/SHE], is quite different from the experimental data of Vasil'ev *et al.* [1973VAS/VAS2]. Considering the later experimental data on heat capacity and entropy and the analysis presented below, the review team rejected the value estimated by Bugden and Shelton [1970BUG/SHE].

To explain these discrepancies between the two data sets, a third-law analysis was carried out of the reactions used by Bugden and Shelton [1970BUG/SHE] and concluded that these data were not internally consistent (see Appendix A).

In view of the experimental details given by Vasil'ev *et al.* [1973VAS/VAS2], it is clear that this enthalpy of formation of  $\text{SnCl}_2(\text{cr})$  should be selected as given, whereas the uncertainty appeared too optimistic and was multiplied by 2, resulting in the selected value:

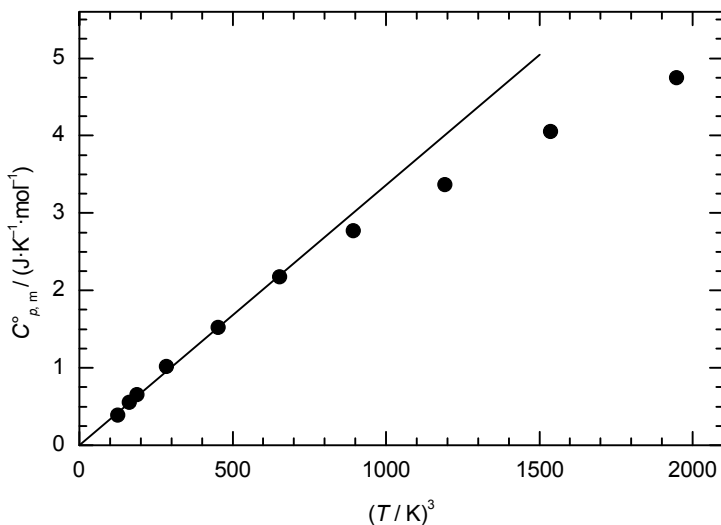
$$\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = -(327.9 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

The heat capacity of  $\text{SnCl}_2(\text{cr})$  in the temperature range of 5 to 305 K was measured by Paukov *et al.* [1979PAU/STE]. The measured values for the sample of high purity ( $w(\text{SnCl}_2) = 99.5\%$ ) in the  $\text{PbCl}_2$ -type rhombic phase are shown in Appendix A. They estimated the accuracy of the measurements as 0.2% at  $T > 25$  K and about 0.5% at  $T < 25$  K. The heat-capacity data of [1979PAU/STE] may be treated by two alternate methods as discussed below. In either case, we may separate the data in two sets; the lowest temperature data below approximately 9 K can be fitted with the Debye's  $T^3$  law function  $C_{p,m}^0 = a \cdot T^3$ . In the  $\text{SnCl}_2(\text{cr})$  case this law is valid up to  $\approx 9$  K (Figure VIII-1). Thus  $a = 0.003365 \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$  can be obtained from  $C_{p,m}^0$  data measured at the 6 lowest temperatures

$$H_m^0(5 \text{ K}) - H_m^0(0 \text{ K}) = \int_0^{5\text{K}} C_{p,m}^0 dT = a \cdot 5^4/4 = 0.5258 \text{ J} \cdot \text{mol}^{-1}$$

$$S_m^0(5 \text{ K}) = \int_0^{5\text{K}} (C_{p,m}^0/T) dT = a \cdot 5^3/3 = 0.1402 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

Figure VIII-1: Low temperature heat capacity of  $\text{SnCl}_2(\text{cr})$ . Experimental data of Paukov *et al.* [1979PAU/STE] with a linear fit (temperature range 5 to 9 K).



For the data between 9 and 304 K, we have the choice of finding a suitable polynomial equation as used in calculation programs such as Chemsage [1998ERI/HAC] or use a spline function (see below). The polynomial equation is:

$$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -4.14601 + 0.68493T/\text{K} + 0.0067938(T/\text{K})^2 \\ - 1.36775 \times 10^{-4} (T/\text{K})^3 + 8.35148 \times 10^{-7} (T/\text{K})^4 \\ - 2.24917 \times 10^{-9} (T/\text{K})^5 + 2.2757 \times 10^{-12} (T/\text{K})^6$$

over the range of temperatures from 9 to 304 K. It becomes negative below 9 K, and has a tendency to oscillate slightly, see Figure VIII-2. This gives us the  $C_{p,m}^{\circ}$  at 298.15 K as  $(77.89 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

An alternative method of arriving at the standard heat-capacity value is to use spline functions for interpolation and integration of low temperature heat-capacity data. Such fits are displayed in Figures VIII-3 to VIII-5.

The heat-capacity data are plotted in three different ways. Figures VIII-3 and VIII-4 show the plots of  $C_p$  as a function of  $T$  and  $\ln T$  respectively, while in Figure VIII-5,  $C_p/T$  is plotted against  $T$ . The three separate fits lead to essentially similar values of  $C_p$  at 298.15 K, demonstrating the robustness of this approach. It may be better to use the spline function fit for low temperature heat-capacity and entropy data for obtaining the value at 298.15 K. The heat capacity  $C_{p,m}^{\circ}(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = (77.89 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  from the polynomial fit may be compared to the value of  $(77.96 \pm 0.31) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  obtained from the spline function fits.

Figure VIII-2: Heat capacity of  $\text{SnCl}_2(\text{cr})$ . Experimental data of Paukov *et al.* [1979PAU/STE] fitted with a polynomial equation (temperature range 9 to 304 K).

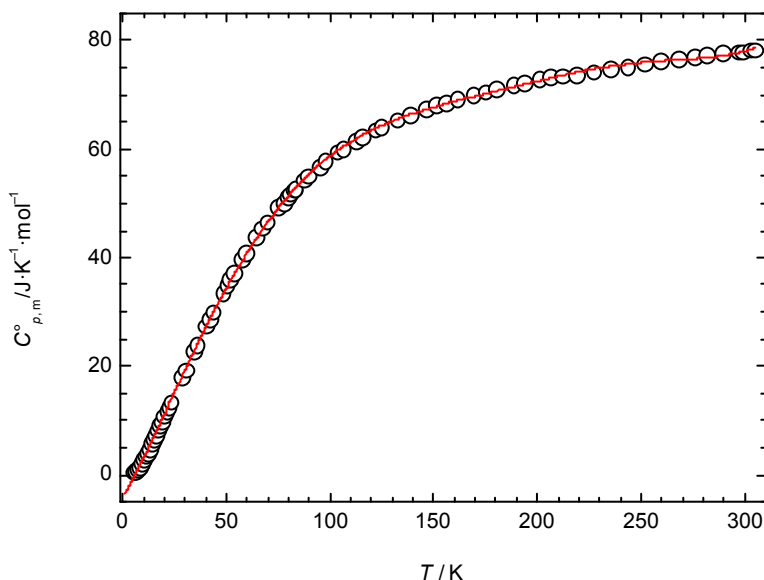


Figure VIII-3: Standard molar heat capacity of  $\text{SnCl}_2(\text{cr})$ . Experimental data of Paukov *et al.* [1979PAU/STE] interpolated with a tension spline (10) function (temperature range 5 to 304 K).

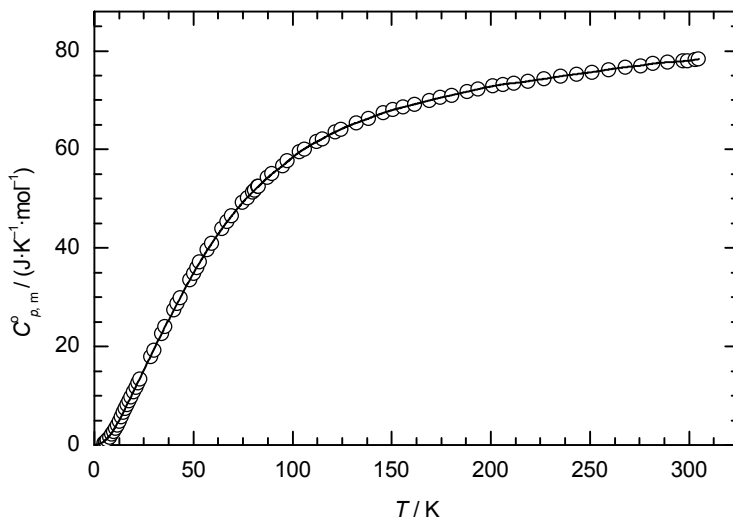


Figure VIII-4: A spline function plot of the standard molar heat capacity of  $\text{SnCl}_2(\text{cr})$ . Experimental data of Paukov *et al.* [1979PAU/STE] fitted using tension spline (10); cubic spline fit leads to essentially the same result. The plot shows heat-capacity data plotted against  $\ln T$ .

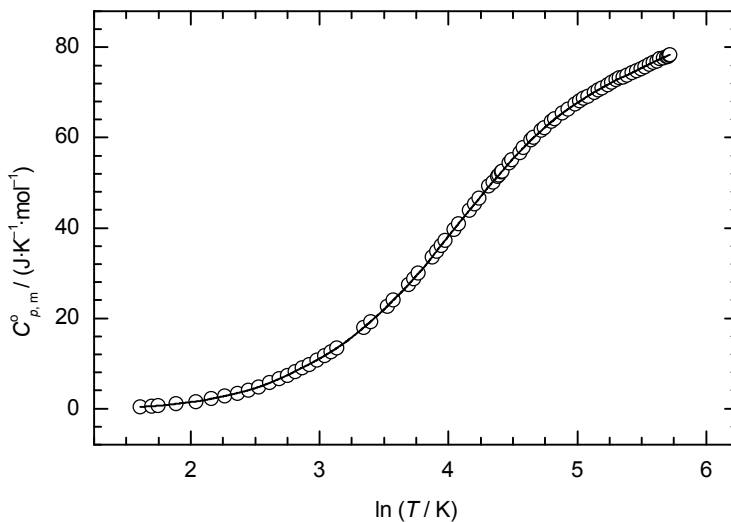
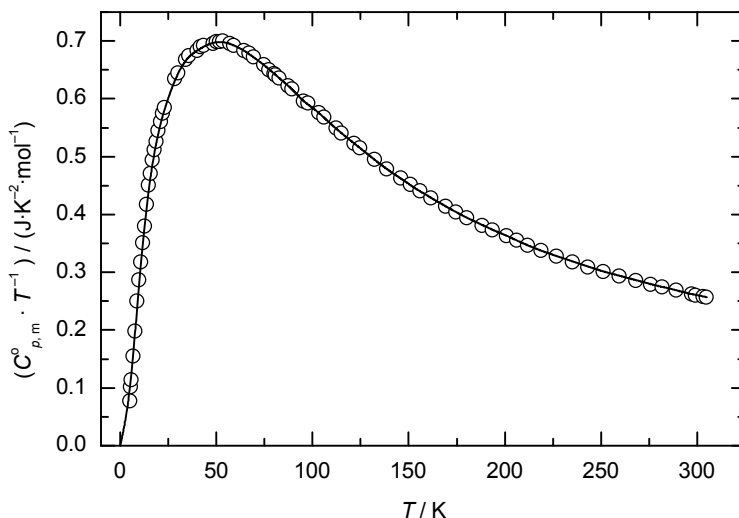


Figure VIII-5: Another plot of the standard molar heat capacity of  $\text{SnCl}_2(\text{cr})$ . Experimental data of Paukov *et al.* [1979PAU/STE] fitted using tension spline (10); cubic spline fit leads to essentially the same result. The plot shows  $C_{p,m}^{\circ}/T$  plotted against  $T$ .



The selected heat-capacity and entropy values are from the analysis of the data of [1979PAU/STE], as shown in Figures VIII-1 to VIII-5.

$$C_{p,m}^{\circ}(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = (77.96 \pm 0.31) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$S_m^{\circ}(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = (133.96 \pm 0.53) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

From these selected values, the Gibbs energy of formation of  $\text{SnCl}_2(\text{cr})$  is calculated to be:

$$\Delta_f G_m^{\circ}(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = -(286.07 \pm 2.20) \text{ kJ} \cdot \text{mol}^{-1}$$

### VIII.1.2.2 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$

Tin(II) chloride dihydrate is a solid with a layered structure. It melts at 313 K.

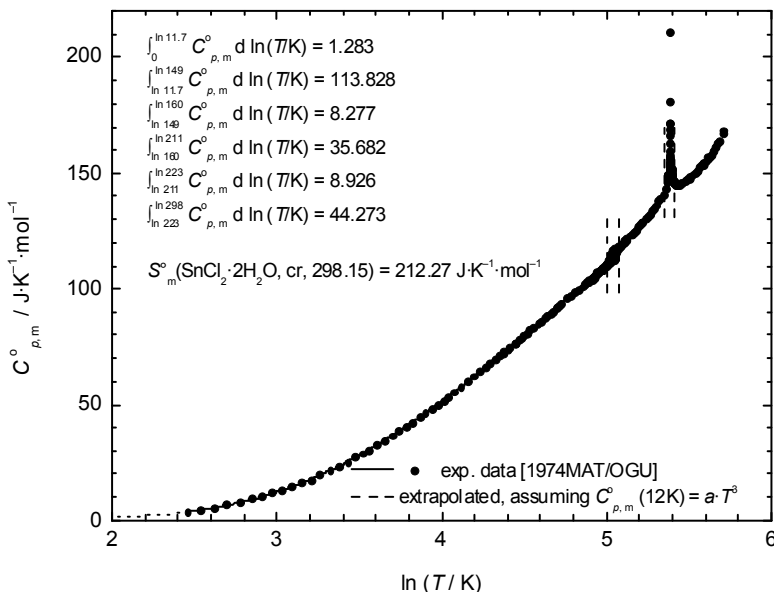
Matsuo *et al.* [1974MAT/OGU] measured calorimetrically the heat capacity of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  crystals from 13 to 300 K. There is a phase transition at 217.94 K, which complicates the measurement at 298.15 K. The solid of high purity was prepared from a slowly cooled melt with a nearly stoichiometric content of water. The overall accuracy of the measurement is estimated as 1% at 20 K and less than 0.3% above 50 K. The data

are tabulated in Appendix A. There was an anomaly noted starting around 150 K and ending at 162 K depending on the thermal history of the sample, the heat-capacity data showing a small inflexion in this temperature range. The cause of this anomaly has not been investigated. A phase transition occurs around 218 K as shown in Figure VIII-6. This is ascribed due to ordering of the hydrogen position. The total entropy change of the transition was estimated to be  $4.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , whereas the exact calculation resulted in  $3.13 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The value of the heat capacity selected by this review is:

$$C_{p,m}^{\circ}(\text{SnCl}_2\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (166.4 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Figure VIII-6: Heat-capacity data of [1974MAT/OGU] showing an anomaly around 150 K and a Phase transition at 218 K.



Due to the complex thermal behaviour of the compound, a calculation of the entropy is not straight forward and implies uncertainties. Using the data from Matsuo *et al.* [1974MAT/OGU] the standard entropy

$$S_m^{\circ}(\text{SnCl}_2\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (212.27 \pm 1.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

can be determined by plotting  $C_p(T)$  against  $\ln(T/K)$ , see Figure VIII-6. This value is selected. Thus, hydration reaction would be accompanied by



an entropy change of  $-61.59 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

From calorimetric dissolution experiments of anhydrous tin(II) chloride and its dihydrate in aqueous HCl containing  $\text{H}_2\text{O}_2$  Vasiliev *et al.* [1973VAS/VAS2] determined the standard enthalpies of formation:

anhydrous tin(II) chloride:

$$\Delta_f H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = - (327.9 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$$

tin(II) chloride dihydrate:

$$\Delta_f H_m^\circ (\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = - (918.26 \pm 1.42) \text{ kJ} \cdot \text{mol}^{-1}$$

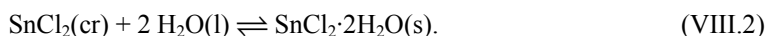
These values are selected.

This yields:

$$\Delta_f G_m^\circ (\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = - (760.68 \pm 1.49) \text{ kJ} \cdot \text{mol}^{-1}$$

From the difference of the formation enthalpies using the same value of the standard enthalpy of formation of water as the authors ( $= -285.829 \text{ kJ} \cdot \text{mol}^{-1}$ ) for Reaction (VIII.1) an enthalpy change of  $-18.7 \text{ kJ} \cdot \text{mol}^{-1}$  is obtained. Combining the entropy and enthalpy change the standard Gibbs energy of hydration becomes  $-0.34 \text{ kJ} \cdot \text{mol}^{-1}$ . However, this value means that regardless of speciation the dihydrate would never exist as an equilibrium phase in aqueous solutions.

According to Section VIII.2.2.1, a solution saturated with tin(II) chloride dihydrate is 12.3 molal at  $25^\circ\text{C}$ . Assuming that this solution would be in equilibrium also with the anhydrous phase the equilibrium constant of Reaction (VIII.2) could be calculated.



From the value of the Gibbs energy of hydration of  $-0.34 \text{ kJ} \cdot \text{mol}^{-1}$  the equilibrium water activity of Reaction (VIII.2) would be 0.934, which is much too high. With the mole fraction of water  $x(\text{w}) = 0.819$  in the saturated solution and even in case of an ideal solution a  $\Delta_r G_m = 2RT \ln(0.819) = -0.99 \text{ kJ} \cdot \text{mol}^{-1}$  would be necessary to enable formation of the dihydrate. Since the real solution has water activity coefficients below 1 the necessary  $\Delta_r G_m$  must be more negative. Also the equilibrium relative humidity above the solid hydrate would be 93.4% according to the Gibbs energy of hydration, which seems to be too high for a bivalent metal halide.

A later calorimetric work of Vasiliev *et al.* [1976VAS/KOK] yields even a less negative value of the hydration enthalpy (approx.  $-(16.7 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$ ) comparing directly the dissolution enthalpies of the anhydrous salt and the dihydrate obtained by formal integration of the  $C_p(T)$  function from the measurements of [1974MAT/OGU]. In conclusion the entropy of the dihydrate is maybe too negative by at least 3 to

$10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Also in relation to the formation of other salt hydrates from the respective anhydrous salts the estimated entropy change of  $-31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  per mole of water in  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  is very negative taking into account the layer structure of the hydrate.

### VIII.1.2.3 Basic tin(II) chloride

#### VIII.1.2.3.1 Composition of basic tin(II) chloride

When concentrated aqueous tin(II) chloride solutions are diluted or alkalisied, white or colourless solid phases precipitate. These precipitates have been repeatedly investigated to determine 1) the chemical composition [1882DIT], [1882DIT2], [1919CAR], [1933HAY], 2) the crystal structure [1963DON/MOS], [1981SCH/NES], [1984ICH/TAK] and 3) the thermodynamic parameters [1930RAN/MUR], [1992EDW/GIL].

Keller [1917KEL] was probably the first to report a natural occurrence of a basic tin(II) chloride in the cavity of a metallic mass found in an Indian cemetery. Corrosion of tin in saline environments results, among others, in chloride-containing tin(II) phases. Matzko *et al.* [1985MAT/EVA] describe a secondary tin mineral, abhurite, found as a corrosion product on ingots of tin from the cargo of a sunken ship. Dunkle *et al.* [2003DUN/CRA] report on abhurite and other secondary tin(II) minerals formed during the corrosion of pewter artefacts [2004DUN/CRA] from another shipwreck. These authors contend that abhurite as well as romarchite,  $\text{SnO}$ , and hydromarchite,  $\text{Sn}_6\text{O}_4(\text{OH})_4$ , form universally during tin corrosion in seawater regardless of the composition of the original pewter artefact. Thus the solubilities of basic tin(II) chloride, tin(II) oxide and tin(II) hydroxide oxide are of considerable interest for the tin corrosion in general and the mobility of tin(II) in particular.

There is, however, a conspicuous discrepancy concerning the formulae ascribed to basic tin(II) chlorides. Keller's [1917KEL] analysis resulted in  $\text{SnCl}_2\cdot\text{SnO}$ . Carson [1919CAR] reported that two distinct basic salt phases were obtained, *viz.*  $3\text{SnCl}_2\cdot 5\text{SnO}\cdot 3\text{H}_2\text{O}$ , and  $2\text{SnCl}_2\cdot 7\text{Sn}(\text{OH})_2$ . Britton [1925BRI2] stated that empirical formulae of basic tin(II) chlorides vary from  $\text{SnCl}_{1.33}(\text{OH})_{0.67}$  at  $\text{pH} \approx 1.9$  to  $\text{Sn}_{0.14}(\text{OH})_{1.86}$  at  $\text{pH} \approx 7$ . Randall and Murakami [1930RAN/MUR] found the composition of their basic chloride to be  $\text{Sn}(\text{OH})\text{Cl}\cdot\text{H}_2\text{O}$ , whereas Hayek [1933HAY] formulated the compound which he obtained as  $\text{Sn}(\text{OH})_2\cdot\text{SnCl}_2$ . Donaldson *et al.* [1963DON/MOS] were able to identify only one definite crystalline basic chloride phase, namely  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ . Ichiba and Takeshita [1984ICH/TAK] suggested that the true composition was  $2\text{SnO}\cdot\text{SnCl}_2\cdot\text{H}_2\text{O}$  and this became, for some time, the stoichiometry which had been attributed to abhurite [1985MAT/EVA]. It is obviously difficult to derive the stoichiometry of basic tin(II) chloride by chemical analysis alone. Thus an amazing variety of stoichiometries for basic tin(II) chloride, based on chemical analyses, have been proposed and are listed in Table VIII-3.



Table VIII-3: Basic tin(II) chlorides.

Reference	Analytically determined stoichiometry	Proposed stoichiometry
[1882DIT2]	$\text{SnCl}_{0.79}\text{O}_{0.61} \cdot 1.23\text{H}_2\text{O}$	$\text{SnCl}_{0.80}\text{O}_{0.60} \cdot 1.2\text{H}_2\text{O}$
[1882DIT2]	$\text{SnClO}_{0.50} \cdot 1.92\text{H}_2\text{O}$	$\text{SnClO}_{0.50} \cdot 2\text{H}_2\text{O}$
[1917KEL]	$\text{SnCl}_{1.01}\text{O}_{0.49} \cdot 0.01\text{H}_2\text{O}$	$\text{SnCl}_{1.00}\text{O}_{0.50}$
[1919CAR]	$\text{SnCl}_{0.75}\text{O}_{0.63} \cdot 0.32\text{H}_2\text{O}$	$\text{SnCl}_{0.75}\text{O}_{0.63} \cdot 0.38\text{H}_2\text{O}$
[1933HAY]	$\text{SnCl}_{0.98}\text{O}_{0.51} \cdot 0.40\text{H}_2\text{O}$	$\text{SnCl}_{1.00}\text{O}_{0.50} \cdot 0.50\text{H}_2\text{O}$
[1963DON/MOS]	$\text{SnCl}_{0.49}\text{O}_{0.75} \cdot 0.76\text{H}_2\text{O}$	$\text{SnCl}_{0.50}\text{O}_{0.75} \cdot 0.75\text{H}_2\text{O}$
[1981SCH/NES], [1965SCH/PEL]	$\text{SnCl}_{0.74}\text{O}_{0.64} \cdot 0.34\text{H}_2\text{O}$	$\text{SnCl}_{0.76}\text{O}_{0.62} \cdot 0.33\text{H}_2\text{O} \triangleq$ $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$
[1882DIT2]	$\text{SnCl}_{0.39}\text{O}_{0.79} \cdot 1.14\text{H}_2\text{O}$	$\text{SnCl}_{0.40}\text{O}_{0.80} \cdot 1.20\text{H}_2\text{O}$
[1919CAR]	$\text{SnCl}_{0.45}\text{O}_{0.77} \cdot 0.07\text{H}_2\text{O}$	$\text{SnCl}_{0.44}\text{O}_{0.78}$
[1981SCH/NES], [1965SCH/PEL]	$\text{SnCl}_{0.43}\text{O}_{0.78}$	$\text{SnCl}_{0.44}\text{O}_{0.78}$ $\triangleq \text{Sn}_9\text{Cl}_4\text{O}_7$

Von Schnering *et al.* [1981SCH/NES] precipitated basic tin(II) chloride from homogeneous solution and refined the structure using single crystal X-ray diffraction data, corrected for absorption and twinning. This determination of the single-crystal structures showed beyond doubt that  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  is the correct composition of the so-called basic tin(II) chloride. Edwards *et al.* [1992EDW/GIL] emphasised that the synthetic phase  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  and the mineral abhurite are identical. Hydrolysis of  $\text{Sn}^{2+}$  in aqueous, chloride-containing solution gives abhurite as the sole tin(II) chloride hydroxide oxide at low pH. The solids obtained in the past, which led to diverse stoichiometries as listed in Table VIII-3 and discussed in the respective Appendix A entries, were almost invariably mixtures of abhurite and a tin(II) chloride oxide formed as an artefact of the synthesis and isolation procedures adopted.

#### VIII.1.2.3.2 Solubility of $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$

Edwards *et al.* [1992EDW/GIL] synthesised  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$  and determined its solubility product at 25 °C, their data were converted to molality basis and re-evaluated using the SIT approach, see Appendix A. In this context the question arose if  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$  was the solubility determining phase in Randall and Murakami's study [1930RAN/MUR].

These authors [1930RAN/MUR] prepared basic tin(II) chloride in two ways.

- 1) A clear solution containing 0.5 M  $\text{SnCl}_2$  + (0.006 – 0.008) M HCl was diluted under nitrogen in the presence of Sn(cr). The precipitate formed was washed by decantation. The suspension of the solid was used for solubility experiments.

- 2) The stock solution of  $\text{SnCl}_2$  was precipitated by a solution containing  $\text{NaCl}$  and  $\text{NaOH}$ , the former having been in large excess. The precipitate was washed free from  $\text{Na}^+$  by decantation.

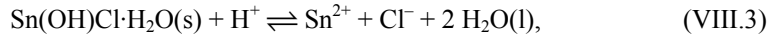
Portions of the thus prepared basic tin(II) chloride were transferred to flasks containing  $\text{HCl}$  solutions or water. The flasks were sealed and rotated at  $(25.00 \pm 0.02)^\circ\text{C}$  from 4 to 78 days. Air-free conditions were maintained throughout the experiment. The equilibrated solutions were filtered off and total dissolved tin(II) and chloride were determined by titration with potassium permanganate solution and as  $\text{AgCl}$  gravimetrically.  $\text{H}^+$  was determined by difference.

For a re-evaluation, columns 1 through 3 of Table VIII-4 have been taken from [1930RAN/MUR], whereas columns 4 through 7 have been calculated using a SIT implemented version of ChemSage taking all Sn(II) chlorido and hydroxido complexes selected by this review into account. In column 8 the expression  $y_{162021} = \log_{10} a_{(\text{Sn}^{2+})} + (16/21) \log_{10} a_{(\text{Cl}^-)} + (20/21) \log_{10} a_{(\text{H}_2\text{O})}$  has been listed.

Table VIII-4: Abhurite, re-evaluation of solubility data on “basic tin chloride” [1930RAN/MUR].

$m_{\text{Sn(II)}}$	$m_{\text{Cl}}$	$m_{\text{H(II) corr.}}$	pH	$\log_{10} a_{\text{Sn}^{2+}}$	$\log_{10} a_{\text{Cl}^-}$	$\log_{10} a_{\text{H}_2\text{O}}$	$y_{162021}$
0.029680	0.14020	0.080840	1.1968	-2.4122	-1.0417	-0.0017	-3.2075
0.030450	0.14074	0.079840	1.2023	-2.4009	-1.0421	-0.0017	-3.1965
0.027300	0.11558	0.060980	1.3149	-2.3758	-1.1204	-0.0014	-3.2307
0.031400	0.15223	0.089430	1.1547	-2.4192	-1.0094	-0.0018	-3.1900
0.010060	0.04789	0.027770	1.6349	-2.5611	-1.4443	-0.0006	-3.6621
0.012340	0.05602	0.031340	1.5864	-2.5114	-1.3868	-0.0007	-3.5687
0.003261	0.01491	0.008388	2.1241	-2.8234	-1.9017	-0.0002	-4.2725
0.002987	0.01227	0.006296	2.2399	-2.8395	-1.9817	-0.0001	-4.3495
0.002981	0.01225	0.006288	2.2405	-2.8402	-1.9824	-0.0001	-4.3507
0.002802	0.01085	0.005246	2.3113	-2.8573	-2.0320	-0.0001	-4.4056
0.002802	0.01085	0.005246	2.3113	-2.8573	-2.0320	-0.0001	-4.4056
0.002824	0.01089	0.005242	2.3115	-2.8546	-2.0307	-0.0001	-4.4019
0.011760	0.07560	0.052080	1.3735	-2.6245	-1.2558	-0.0009	-3.5822
0.014100	0.06790	0.039700	1.4926	-2.5068	-1.3108	-0.0008	-3.5063
0.006407	0.03294	0.020126	1.7654	-2.6712	-1.5860	-0.0004	-3.8800
0.023290	0.10949	0.062910	1.3002	-2.4329	-1.1333	-0.0013	-3.2976
0.008168	0.03731	0.020974	1.7504	-2.5924	-1.5421	-0.0004	-3.7677
0.009081	0.03879	0.020628	1.7584	-2.5547	-1.5300	-0.0005	-3.7209
0.009248	0.03825	0.019754	1.7767	-2.5434	-1.5367	-0.0004	-3.7146
0.009907	0.04363	0.023816	1.6991	-2.5443	-1.4835	-0.0005	-3.6751
0.008825	0.04023	0.022580	1.7203	-2.5759	-1.5132	-0.0005	-3.7293

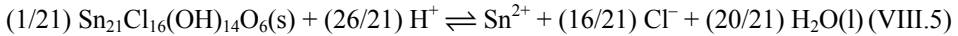
If the dissolution process is governed by Reaction (VIII.3):



Eq. (VIII.4) follows

$$\log_{10} a_{(\text{Sn}^{2+})} + \log_{10} a_{(\text{Cl}^-)} + 2 \log_{10} a_{(\text{H}_2\text{O})} = \log_{10} {}^*K_{s,111}^{\circ} - \text{pH} \quad (\text{VIII.4})$$

and the left-hand side of Eq. (VIII.4) should be a linear function of pH with slope =  $-1.00$ . Figure VIII-7 shows that this is not the case. A least squares analysis of the data of Randall and Murakami [1930RAN/MUR] results in a slope of  $-(1.238 \pm 0.083)$ , which is by chance the value expected if Reaction (VIII.5) and Eq. (VIII.6)



$$\log_{10} a_{\text{Sn}^{2+}} + (16/21) \log_{10} a_{\text{Cl}^-} + (26/21) \log_{10} a_{\text{H}_2\text{O}} = \log_{10} {}^*K_{s,16202621} - (26/21)\text{pH} \quad (\text{VIII.6})$$

govern the dissolution process.

Figure VIII-7: Solubility of basic tin(II) chloride, abhurite, according to Reactions (VIII.3) and (VIII.5). (●):  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ , theoretical slope =  $-1.238$ , experimental data of [1930RAN/MUR]; (○):  $\text{Sn(OH)Cl(s)}$ , theoretical slope =  $-1.0$ , experimental data of [1930RAN/MUR]; (▼):  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ , experimental data of [1992EDW/GIL]; solid line: least squares analysis, slope =  $-(1.222 \pm 0.018)$ ; dotted line: slope =  $-(1.238 \pm 0.018)$ ; dash dot line, intercept =  $-2.403$ .

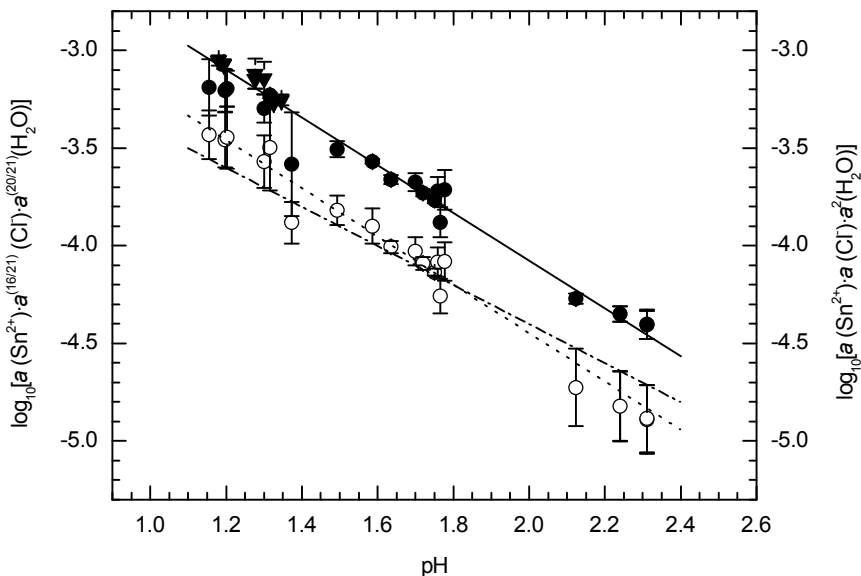


Figure VIII-7 shows that the recalculated data of [1930RAN/MUR] and [1992EDW/GIL] fall closely onto the same straight line.

The least squares analysis of the left-hand side of Eq. (VIII.6) vs. pH using both data sets results in a slope of  $-(1.222 \pm 0.018)$ , which overlaps with the theoretical value  $-26/21 = -1.238$ .

With the theoretical slope, the following solubility constant was derived:  $\log_{10}^* K_{s16202621} = -(1.62 \pm 0.16)$  which in turn leads to

$$(1/21) \Delta_f G_m^\circ (\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6, \text{cr}, 298.15 \text{ K}) = -(362.46 \pm 0.97) \text{ kJ}\cdot\text{mol}^{-1},$$

this value has been selected.

### VIII.1.3 Solid bromides

$\text{SnBr}_2(\text{cr})$  is a white or pale yellow solid. It melts at 507 K [1992BRU/WAL] and boils at 893 K.  $\text{SnBr}_2$  forms numerous hydrates such as  $3\text{SnBr}_2\cdot\text{H}_2\text{O}$ ,  $2\text{SnBr}_2\cdot\text{H}_2\text{O}$  and  $6\text{SnBr}_2\cdot 5\text{H}_2\text{O}$ .

$\text{SnBr}_4(\text{cr})$  is white and crystallises in the monoclinic system and melts at 302.5 K [1927BIL/JEE], [1956KAP/KES] and boils at 479 K.

#### VIII.1.3.1 $\text{SnBr}_2(\text{cr})$

Bugden and Shelton [1973BUG/SHE] determined the standard Gibbs energies of formation in the temperature range of 298 to 500 K from potential measurements on the cells  $\text{M} | \text{MBr}_n | \text{PbBr}_2 | \text{AgBr} | \text{Ag}$  [ $\text{M} = \text{Pb}$  ( $n = 2$ ),  $\text{Sn}$  ( $n = 2$ ), or  $\text{Cu}$  ( $n = 1$ )]. For  $\text{SnBr}_2(\text{cr})$  the equation  $\Delta_f G_m^\circ (\text{SnBr}_2, \text{cr}, T)/\text{kJ}\cdot\text{mol}^{-1} = -278.4 - 0.1279 T/\text{K}$  was fitted to the data. No errors were assigned. These authors used the second law of thermodynamics to calculate the standard heat of formation at 298.15 K with  $\text{Br}_2(1)$  as the reference state,  $\Delta_f H_m^\circ (\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = -247.0 \text{ kJ}\cdot\text{mol}^{-1}$ . This is an example of one of the several enthalpy data for  $\text{SnBr}_2(\text{cr})$  in literature, which vary over a wide range ( $-243.51 \text{ kJ}\cdot\text{mol}^{-1}$  in [1968WAG/EVA] and  $-266.10 \text{ kJ}\cdot\text{mol}^{-1}$  in [1963BRE/SOM]). The measured enthalpy from solution calorimetry by [1977STE/KOK] led to  $\Delta_f H_m^\circ (\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = -(252.92 \pm 2.34) \text{ kJ}\cdot\text{mol}^{-1}$ , which was adopted in [1992BRU/WAL]. Stenin *et al.* [1977STE/KOK] measured the enthalpies of the reactions of Sn,  $\text{Br}_2$  and  $\text{SnBr}_2$  with solution of bromine in  $\text{CCl}_4$ . Gurvich and Veyts [1991GUR/VEY] recommended  $\Delta_f H_m^\circ (\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = -(253.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ . Their value accounts for the differences among the determinations of Stenin *et al.* [1977STE/KOK] and Bugden and Shelton [1973BUG/SHE]. Considering the larger uncertainties associated with cell potential measurements, the value of the enthalpy of formation obtained by Stenin *et al.* is selected here:

$$\Delta_f H_m^\circ (\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = -(252.9 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

The value recommended by [1991GUR/VEY] falls within the error limits.

Berezovskii *et al.* [1980BER/STE] measured the heat capacity of SnBr<sub>2</sub>(cr) in the 5.5 to 322 K temperature range, and reported 87 points (see Appendix A). For standard conditions the data are  $C_{p,m}^{\circ}(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = (78.97 \pm 0.16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_m^{\circ}(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = (153.0 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Brumleve *et al.* [1992BRU/WAL] reviewed the molar heat capacities for the condensed phases of SnBr<sub>2</sub>. Pankratz [1984PAN] extrapolated the low-temperature measurements of [1980BER/STE]. Gardner and Preston [1991GAR/PRE] determined the molar heat capacity of the solid, at  $T = 350$  to  $500 \text{ K}$ , and the liquid, at  $T = 520$  to  $800 \text{ K}$ , using differential scanning calorimetry. The heat capacity over the temperature range of  $350$  to  $800 \text{ K}$  is given by:  $C_{p,m}^{\circ}(\text{SnBr}_2, \text{l}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (70.18 \pm 0.33) + (0.04933 \pm 0.00107) T/\text{K}$ . Their extrapolated value of the heat capacity at  $298.15 \text{ K}$  is  $78.60 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Brumleve *et al.* [1992BRU/WAL] further combined the data from their own study with that of [1991GAR/PRE] to calculate the molar heat capacity of the solid from  $298.15$  to  $507 \text{ K}$  and of the liquid from  $507$  to  $1000 \text{ K}$ . The parameters for the polynomials describing the temperature variation of the molar heat capacities are listed in Table VIII-5.

Table VIII-5: Parameters for the temperature variation of the molar heat capacity of SnBr<sub>2</sub> using the equation (after [1992BRU/WAL]):  $C_{p,m}^{\circ}(\text{SnBr}_2, (\text{s}, \text{l}, \text{or g}), T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = A + B T/\text{K} + C (T/\text{K})^2 + D (T/\text{K})^{-2}$  for condensed-phase species ( $298 \leq T/\text{K} \leq 1000$ ) and for the gas ( $298 \leq T/\text{K} \leq 6000$ ).  $p^{\circ} = 101325 \text{ Pa}$ .

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
SnBr <sub>2</sub> (s)	$4.1097 \times 10^1$	$1.2158 \times 10^{-1}$	$-6.3618 \times 10^{-5}$	$6.4755 \times 10^5$
SnBr <sub>2</sub> (l)	$8.8328 \times 10^1$	$-4.6988 \times 10^{-3}$	$4.0879 \times 10^{-5}$	$-5.4090 \times 10^4$
SnBr <sub>2</sub> (g)	$5.8169 \times 10^1$	$1.5400 \times 10^{-5}$	$-1.7100 \times 10^{-9}$	$-1.5911 \times 10^5$

Brumleve *et al.* [1992BRU/WAL] adopted the entropy data from [1980BER/STE] for the solid as  $153.00 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ; they also calculated the entropy for the liquid and gas phases ( $176.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $328.764 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  respectively) employing the third-law procedure, the heat-capacity data as in Table VIII-5 and spectroscopic data. Error estimates are not given.

The values of the heat capacity and entropy of SnBr<sub>2</sub>(cr) selected by this review are from Berezovskii *et al.* [1980BER/STE]:

$$C_{p,m}^{\circ}(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = (78.97 \pm 0.16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m^{\circ}(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = (153.0 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^\circ(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = -(237.88 \pm 2.30) \text{ kJ}\cdot\text{mol}^{-1}.$$

### VIII.1.3.2 SnBr<sub>4</sub>(cr)

SnBr<sub>4</sub> solidifies as a β-phase below the melting temperature of 302.25 K [1983BER/STE] and undergoes other phase transitions at 287 K [1956KAP/KES], [1983BER/STE] and 267 K [1927BIL/JEE]. Gurvich and Veyts [1991GUR/VEY] adopted a value of the enthalpy of formation as of  $\Delta_f H_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = -(388.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$ . This is based on the results of the measurements carried out by Stenin *et al.* [1977STE/KOK], who measured calorimetric data for the reaction  $\text{Sn}(\text{cr}) + 2 \text{Br}_2(\text{l}) \rightleftharpoons \text{SnBr}_4(\text{cr})$ . The enthalpies of reactions of Sn, Br<sub>2</sub> and SnBr<sub>4</sub> with a solution of bromine in CCl<sub>4</sub> were measured with the resulting enthalpy of formation of  $-(390.20 \pm 1.98) \text{ kJ}\cdot\text{mol}^{-1}$ . Mikler and Janitsch [1975MIK/JAN] determined the enthalpy change of the reaction between Br<sub>2</sub>(l) and Sn(cr) in CS<sub>2</sub> as solvent forming SnBr<sub>4</sub>(cr) at 298.15 K using a calorimetric method and found it to be  $-(374.0 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$ . They further determined the enthalpy of solution of SnBr<sub>4</sub>(cr) in CS<sub>2</sub> as  $(11.9 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$ . These data were then combined to arrive at the enthalpy of formation for the compound as  $-(386.1 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$ . Substituting this figure in the thermochemical cycle as used for calculating the heat of formation of SnBr<sub>4</sub>(cr) gives  $-520.07 \text{ kJ}\cdot\text{mol}^{-1}$  for the standard enthalpy of formation of SnCl<sub>4</sub>(l) [1975MIK/JAN], which is close to the value selected by this review  $\Delta_f H_m^\circ(\text{SnCl}_4, \text{l}, 298.15 \text{ K}) = -(517.0 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ . The datum for SnBr<sub>4</sub>(cr) as adopted in [1991GUR/VEY] has a large error which covers all the determinations and this review also selects this value despite the large error:

$$\Delta_f H_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = -(388.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

Berezovskii *et al.* [1983BER/STE] measured the heat capacity of tin tetrabromide (monoclinic to 287 K) at 112 points in the temperature range 6.66 to 336.2 K in a vacuum adiabatic calorimeter with a nickel bulb [1978BER/PAU], see Figure VIII-8. The experimental data  $T, C_{p,m}^\circ$  are listed in Table A-44.

The heat capacity of the monoclinic phase can be fitted with the following equation in the temperature range of 7 to 287 K:

$$C_{p,m}^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/\text{K} + c (T/\text{K})^2 + d (T/\text{K})^{-1} + e (T/\text{K})^{-2} + f (T/\text{K})^{-0.5}$$

where  $a = (174.35 \pm 3.60)$ ,  $b = (0.012684 \pm 0.014197)$ ,  $c = (5.0467 \pm 27.1990) \times 10^{-6}$ ,  $d = (1002.9 \pm 90.3)$ ,  $e = (492.24 \pm 199.79)$  and  $f = -(856.07 \pm 32.96)$ .

The heat capacity for this phase (metastable) at 298.15 is  $132.38 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$ .

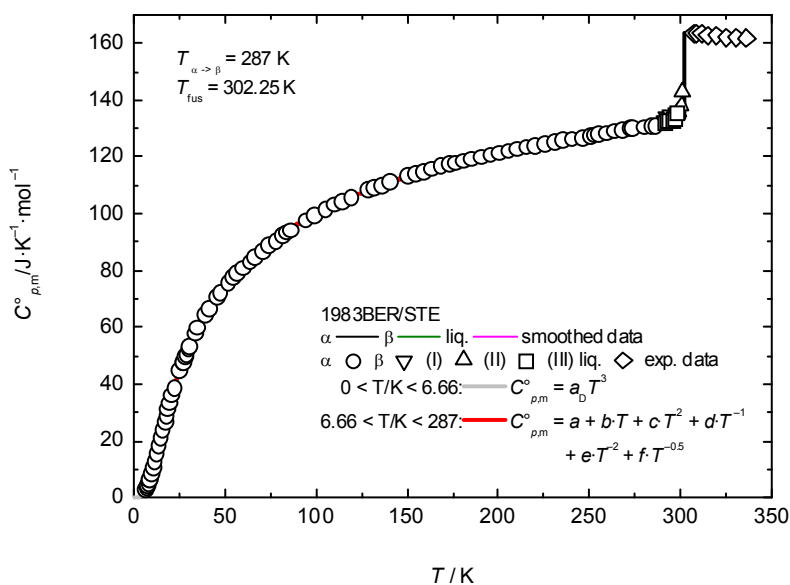
The measured heat capacity for the  $\beta$ -phase at 298.15 K is  $(133.3 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The entropy of  $\beta$ - $\text{SnBr}_4$  at 298.15 K has been obtained by adding the following parts:

$$S_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = C_{p,m}(T_1)/3 + \int_{T_1}^{T_{\text{trs}}} (C_{p,m}/T) dT + \Delta_\alpha^\beta H_m^*/T_{\text{trs}} + \int_{T_{\text{trs}}}^{T_{\text{ref}}} (C_{p,m}/T) dT$$

where  $T_1 = 6.66$ ,  $T_{\text{trs}} = 287$  and  $T_{\text{ref}} = 298.15$  K, see Appendix A entry [1983BER/STE]

$$S_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = (260.0 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Figure VIII-8: Heat capacity data for  $\text{SnBr}_4(\text{cr})$  as measured by Berezovskii *et al.* [1983BER/STE].



The data selected by this review for  $\text{SnBr}_4(\text{cr})$  are:

$$C_{p,m}^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = (133.3 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = (260.0 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

which yields:

$$\Delta_f G_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = - (359.50 \pm 3.00) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VIII.1.4 Solid iodides

### VIII.1.4.1 Introduction

SnI<sub>2</sub> is a red or red-orange colored crystalline solid (monoclinic) with a melting point of 589 K, a boiling point of 993 K [1984GRE/EAR].

SnI<sub>4</sub>(cr) is a brown or yellow-brown crystalline solid (cubic) with a melting point of 417 K, a boiling point of 621 K [1984GRE/EAR].

### VIII.1.4.2 SnI<sub>2</sub>(cr)

Mikler and Janitsch [1975MIK/JAN2] measured the heat of the reaction SnI<sub>2</sub>(s) + I<sub>2</sub>(s) + 4045CS<sub>2</sub>(l) ⇌ [SnI<sub>4</sub>; 4045CS<sub>2</sub>](sln) to be  $-(41.12 \pm 0.55)$  kJ·mol<sup>-1</sup> by isoperibol solution calorimetry. The heat of formation of SnI<sub>2</sub>(cr) was calculated by using the literature data for SnI<sub>4</sub> previously measured by Mikler [1973MIK]. The enthalpy of formation at 298 K for SnI<sub>2</sub>(cr) is determined to be  $-(153.9 \pm 1.40)$  kJ·mol<sup>-1</sup>.

Stenin *et al.* [1975STE/KOK] determined the standard enthalpy of formation of SnI<sub>2</sub>(cr) by direct calorimetry in the range 332 to 593 K (20 points). The heats of dissolution of Sn(cr), SnBr<sub>2</sub>(cr), SnBr<sub>4</sub>(cr), Br<sub>2</sub>(l) in (CCl<sub>4</sub> + Br<sub>2</sub> + SnBr<sub>4</sub>) and the heats of dissolution of Sn(cr), SnI<sub>2</sub>(cr), SnI<sub>4</sub>(cr), I<sub>2</sub>(cr) in (CCl<sub>4</sub> + I<sub>2</sub> + SnI<sub>4</sub>) were measured by a calorimetric method. A high purity sample was used for SnI<sub>2</sub>(monoclinic) and the enthalpy of formation at 298.15 K is determined as  $\Delta_f H_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = -(152.1 \pm 2.0)$  kJ·mol<sup>-1</sup>.

A second calorimetric measurement following the same method is by Mikler [1973MIK] which resulted in  $\Delta_f H_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = -(153.9 \pm 1.4)$  kJ·mol<sup>-1</sup>.

We accept the data based on [1977STE/KOK] and [1975MIK/JAN2]. Thus the selected value of the enthalpy of formation of SnI<sub>2</sub>(cr) is:

$$\Delta_f H_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = -(153.3 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

A third calorimetric measurement by Cartwright and Woolf (1976) was not considered because of the missing experimental details.

Anisimov *et al.* [1974ANI/ZHA] determined the heat capacity of SnI<sub>2</sub>(cr) (11.7 to 312.7 K) on a sample of high purity with an accuracy of the measurements estimated as lying within 0.1 to 0.2% (see Appendix A). Their data were fitted by this review to the equation:  $[C_{p,m}^\circ]_{11.7\text{K}}^{312.7\text{K}}(\text{SnI}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (76.62 + 0.0228 T/\text{K} - 1459/(T/\text{K}) + 8107/(T/\text{K})^2)$ , resulting in  $C_{p,m}^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = (78.62 \pm 0.16)$  J·K<sup>-1</sup>·mol<sup>-1</sup>. The equation is given only if any limited extrapolation is required. For the standard state data, this review selects:

$$C_{p,m}^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = (78.45 \pm 0.16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$



$$S_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = (167.8 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The Gibbs energy of formation of  $\text{SnI}_2(\text{cr})$  is calculated to be:

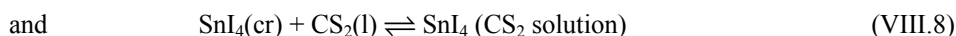
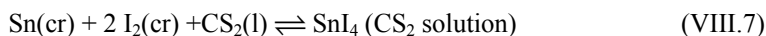
$$\Delta_f G_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = -(153.44 \pm 2.32) \text{ kJ}\cdot\text{mol}^{-1}.$$

Gardner and Preston [1991GAR/PRE] used DSC to determine the heat capacity of the halides. The method results in data which are estimated to have an accuracy of  $\pm 2\%$  between 300 and 1000 K. Such data were fitted to an equation ( $a + bT$ ) with the coefficients  $a = (67.23 \pm 0.22)$  and  $b = (0.03528 \pm 0.00047)$  over the temperature range of 350 to 590 K. The extrapolated value at 298.15 is  $77.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , similar to the datum selected above.

### VIII.1.4.3 $\text{SnI}_4(\text{cr})$

Stenin *et al.* [1975STE/KOK] measured the heats of dissolution of  $\text{Sn}(\text{cr})$ ,  $\text{SnI}_2(\text{cr})$ ,  $\text{SnI}_4(\text{cr})$ ,  $\text{I}_2(\text{cr})$  in  $(\text{CCl}_4 + \text{I}_2 + \text{SnI}_4)$  by the calorimetric method and determined the standard enthalpy of formation in the range 330 to 414 K (20 points) for the compound  $\text{SnI}_4(\text{cr})$ ; the uncertainty in the enthalpy measurements was estimated as 0.6% at 330 to 370 K and 0.3% at  $T > 370$  K. The enthalpy at 298.15 K is determined as  $\Delta_f H_m^\circ(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = -(206.1 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ .

Mikler [1973MIK] measured the enthalpy change at 298.15 K for the reactions



with  $\Delta_f H_m^\circ(\text{VIII.7}) = -(195.39 \pm 1.26) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^\circ(\text{VIII.8}) = (13.39 \pm 0.42) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. This results in  $\Delta_f H_m^\circ(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = -(208.8 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ .

The selected enthalpy of formation of  $\text{SnI}_4(\text{cr})$  must be determined by the two calorimetric data that are found to be consistent. Both experiments involve the dissolution reactions in  $\text{CS}_2$ . Taking the weighted mean of the two values and reassigning uncertainties by multiplying both  $\sigma$  by 2 yields:

$$\Delta_f H_m^\circ(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = -(208.0 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

A third calorimetric measurement by Cartwright and Woolf [1976CAR/WOO] was not considered because of the missing experimental details.

Anisimov *et al.* [1974ANI/STE] determined the heat capacity of cubic  $\text{SnI}_4$  in the temperature range of 11.5 to 308 K on a sample of high purity with an accuracy of the measurements estimated as lying within 0.1 to 0.2%. The values are reported in Appendix A. The data were fitted by this review to the equation:  $[C_{p,m}^\circ]_{11.5\text{K}}^{308\text{K}}(\text{SnI}_4, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 121.2 + 6.190 \times 10^{-2} T/\text{K} - 2113/(T/\text{K}) + 10731/(T/\text{K})^2$  for limited extrapolation.

The data of Anisimov *et al.* result in the selected values of the heat capacity and entropy of  $\text{SnI}_4(\text{cr})$ :

$$C_{p,m}^{\circ}(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = (131.96 \pm 0.26) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = (282.71 \pm 1.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

which yields:

$$\Delta_f G_m^{\circ}(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = -(207.78 \pm 2.23) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VIII.2 Solubility of tin halides in aqueous systems

All the tin(II) halides are very soluble due to strong complex formation. Therefore solubility constants can only be derived in combination with a model of the Gibbs excess energy of the solution valid to high concentrations.

### VIII.2.1 Solubility of tin fluorides

#### VIII.2.1.1 $\text{SnF}_2(\text{cr})$

$\text{SnF}_2(\text{cr})$  exists in three forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ , see Section VIII.1.1.1).  $\alpha$ - $\text{SnF}_2$  and  $\beta$ - $\text{SnF}_2$  can be crystallised from aqueous solutions [1965DON/OTE].

$\text{SnF}_2(\text{cr})$  is highly soluble in water [1952NEB/MUH], [1963BEA]. Solubility data listed in [1972GME] could not be found in the reference cited [1952NEB/MUH].

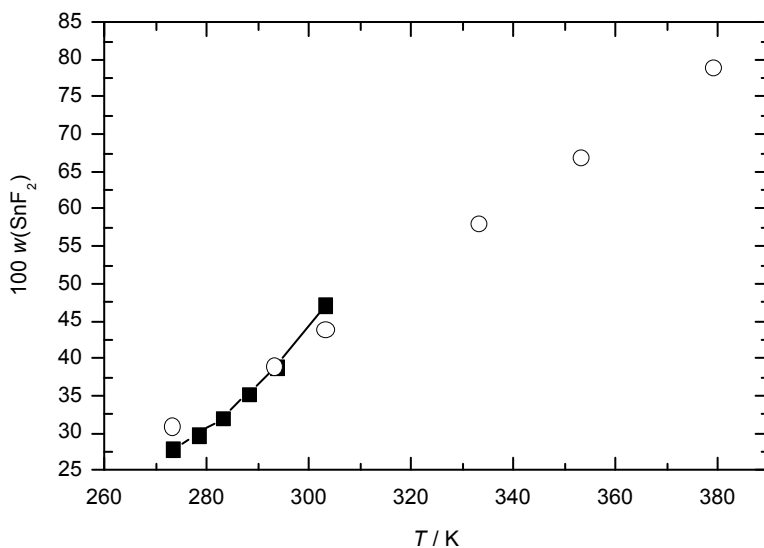
Table VIII-6: Solubility data of  $\text{SnF}_2(\text{cr})$  given in [1972GME].

$T/\text{K}$	273.16	278.26	283.02	288.20	293.51	303.16
$w(\text{SnF}_2)$	0.2789	0.2977	0.3215	0.3535	0.3885	0.4710

In [1963HEF] a temperature-solubility plot is given with data from [1961TEC]. Data read from graphic with uncertainties of ( $\pm 1 \text{ K}$  and  $\pm 1\%$ ) are plotted in Figure VIII-9. The plot of [1963HEF] data is almost linear, which is atypical for highly soluble substances over a range of 100 K. Solutions containing  $w(\text{SnF}_2)$  from 0.05 to 0.10 remain clear for several hours. At concentrations below 1%  $\text{SnF}_2$  hydrolytic precipitation is observed instantaneously [1963HEF].

The density of a saturated solution at 298 K is reported as  $1.51 \text{ g}\cdot\text{cm}^{-3}$  [1963HEF]. [1954NEB/BAS] note a solubility at 298 K of 55 mass-%, which is much higher than can be read from Figure VIII-9.

Figure VIII-9: Temperature dependence of  $\text{SnF}_2(\text{cr})$  solubility. Experimental data from: ■: [1963BEA] and ○: [1963HEF].



Solubility in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  between 263.7 and 303.15 K has been investigated by [1963BEA]. Selected data from this reference are listed in [1972GME] at 273.15 K. In Figure VIII-10 the solubility isotherm in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  is plotted as given by [1963BEA] at  $t = 0^\circ\text{C}$  (data at extremely high HF contents with  $\text{SnF}_2\cdot 2\text{HF}$  as solid phase are omitted). An enlargement of the lower part of the solubility isotherm together with data at other temperatures are plotted in Figure VIII-11. The shaded area defines the scatter of the data for  $0^\circ\text{C} < t < 30^\circ\text{C}$ . From the plot of all data at  $t = 25^\circ\text{C}$  a solubility of  $w(\text{SnF}_2) = 40 - 50\%$  or  $m(\text{SnF}_2) = 4.5 - 9.0 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$ , respectively, can be estimated. This is in agreement with the data of [1963HEF]. Using the complex formation constants of this review and  $\Delta_f G_m^\circ$  of  $\text{HF}(\text{aq})$ ,  $\text{HF}_2^-$  and  $\text{F}^-$  of Table IV-1 (auxiliary data) a Gibbs energy of formation  $\Delta_f G_m^\circ$  of  $\text{SnF}_2(\text{s})$  was estimated by stepwise simulation of solubility as shown in Figure VIII-11. Values between  $-640 \text{ kJ}\cdot\text{mol}^{-1}$  to  $-638 \text{ kJ}\cdot\text{mol}^{-1}$  cover the experimental data area. Since the simulation results depend on the formation constants  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  of the fluoro complexes the sensitivity on the simulated solubilities were tested. Changing  $\beta_1$  and  $\beta_2$  by one order of magnitude and  $\beta_3$  by three orders of magnitude, all in the direction to higher values enhances the solubility from  $4.0 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$  to  $8.9 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$ , which is still well within the range of experimental uncertainty. Thus it is concluded that  $-(639.0 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  can be accepted as a first estimate of  $\Delta_f G_m^\circ$  for  $\text{SnF}_2(\text{s})$ .

Figure VIII-10: Solubility isotherm in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  at  $t = 0^\circ\text{C}$  (■:  $\text{SnF}_2\cdot\text{H}_2\text{O}$ ; ○:  $\text{SnF}_2$ ).

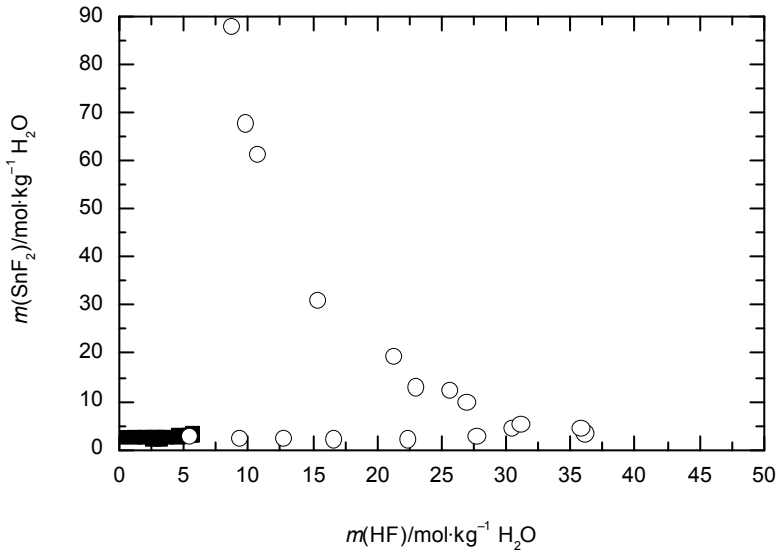
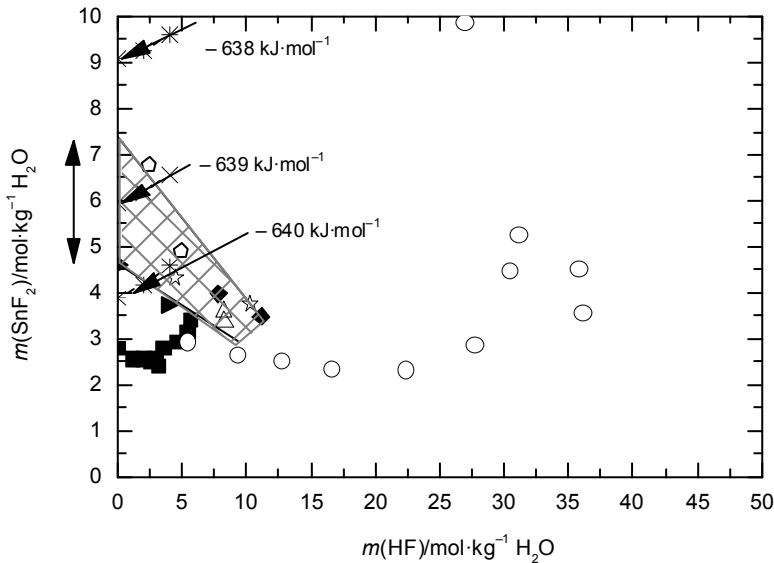


Figure VIII-11: Solubilities in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  at different temperatures. The experimental data are reported in Table A-17. The solubility range for  $t = 5$  to  $30^\circ\text{C}$  is shown by the shaded area; arrows point to calculated solubilities with  $\Delta_f G_m^\circ$  of  $\text{SnF}_2(\text{s})$  as given. (■:  $\text{SnF}_2\cdot\text{H}_2\text{O}$  at  $0^\circ\text{C}$ ; ○:  $\text{SnF}_2$  at  $0^\circ\text{C}$ ; △:  $\text{SnF}_2$  at  $5^\circ\text{C}$ ; ◆:  $\text{SnF}_2$  at  $9.9^\circ\text{C}$ ; ◇:  $\text{SnF}_2$  at  $30^\circ\text{C}$ ; ☆:  $\text{SnF}_2$  at  $15.4^\circ\text{C}$ ; ▲:  $\text{SnF}_2$  at  $20^\circ\text{C}$ ).

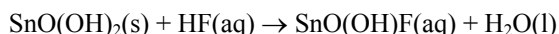


**VIII.2.1.2 SnF<sub>4</sub>(s)**

This compound undergoes an exothermic dissolution in water, and oxide hydrates precipitate. No hydrates of SnF<sub>4</sub> are obtained [1918FUR], [1912WOL].

**VIII.2.1.3 SnO(OH)F(s)**

In [1972GME] it is reported that SnO(OH)F forms from acidic NaF solution and excess of SnO(OH)<sub>2</sub>. In the original paper, Kleiner and Vasilenko [1960KLE/VAS] investigated the solubility of SnO(OH)<sub>2</sub> as a function of fluoride concentration and pH. The solubility of SnO(OH)<sub>2</sub> is entirely controlled by the formation of basic fluoro complexes. In absence of fluoride the solubility in acidic and basic solutions is below  $5 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ . Employing these facts an equilibrium constant  $K = (1.05 \pm 0.09) \times 10^{-2}$  was derived for the reaction



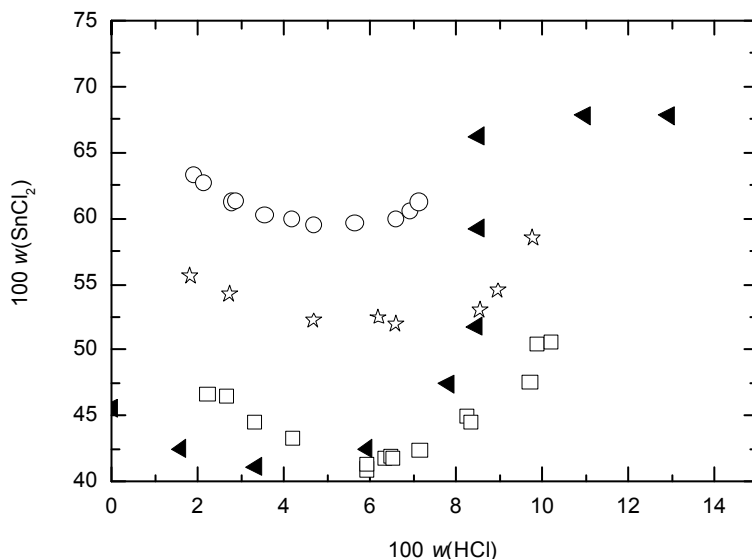
at  $t = (20 \pm 1) \text{ }^\circ\text{C}$  and  $\text{pH} = 1.0$  in  $\text{HNO}_3$  [1960KLE/VAS] (see Appendix A). Standard Gibbs energy of formation is reported as  $\Delta_f G_m^\circ(\text{SnO(OH)F, s, 298.15 K}) = -188.5 \text{ kcal}\cdot\text{mol}^{-1}$  [1968WAG/EVA] =  $-788.68 \text{ kJ}\cdot\text{mol}^{-1}$ .

**VIII.2.2 Solubility of tin chlorides****VIII.2.2.1 SnCl<sub>2</sub>(s)**

Tin(II) chloride dissolves in water undergoing hydrolysis. Ryss and Turkhan [1947RYS/TUR] investigated the solubility in the system SnCl<sub>2</sub>-HCl-H<sub>2</sub>O at 278, 288 and 298 K (Figure VIII-12). The authors listed also the data from [1888ENG].

The solubility curve of Engel [1888ENG] shows a behaviour which is different from the curve obtained by Ryss and Turkhan [1947RYS/TUR]. Engel gave no information about the solid phase. Ryss and Turkhan determined the composition of the solid phase with the Schreinemakers method and found in all cases SnCl<sub>2</sub>·2H<sub>2</sub>O. The dihydrate melts at 39 – 40.5 °C, it is not known whether it melts congruently or incongruently [1947RYS/TUR], [1914FUJ]. Crystallisation of the dihydrate was also observed in the system SnCl<sub>2</sub>-KCl-H<sub>2</sub>O [1914FUJ]. Obviously, there exists also a monohydrate SnCl<sub>2</sub>·H<sub>2</sub>O, which forms during thermal dehydration of the dihydrate at 80 to 120 °C [1883DIT], [1959CUE/HAR], [1961KAM/GRD].

Figure VIII-12: Solubility in the system  $\text{SnCl}_2\text{-HCl-H}_2\text{O}$  as a function of the hydrochloric acid concentration. Experimental data from [1947RYS/TUR] ( $\square$ : 5 °C;  $\star$ : 15 °C;  $\circ$ : 25 °C); and from [1888ENG] ( $\blacktriangleleft$ : 0 °C).



### VIII.2.2.2 $\text{SnCl}_2(\text{s}) - \text{SnF}_2(\text{s})$

Compounds  $\text{SnCl}_2 \cdot \text{SnF}_2$  and  $\text{SnCl}_2 \cdot 3\text{SnF}_2$  can be crystallised from aqueous solutions with melting points between 185 – 195 °C and 179 – 181 °C, respectively [1954NEB/BAS], [1969DON/SEN]. But no thermodynamical data are available.

### VIII.2.2.3 $\text{SnCl}_4(\text{l})$

At room temperature  $\text{SnCl}_4$  is a liquid with a melting point of 240 K and a boiling point of 387 K. In saturated aqueous solutions formation of the hydrates  $\text{SnCl}_4 \cdot n\text{H}_2\text{O}$  ( $n = 2, 3, 4, 5, 8, 9$ ) has been reported [1972GME]. Stability ranges in contact with solution extend up to 83 °C [1891MEY]. The dihydrate should be better denoted as an acid  $\text{H}_2[\text{SnCl}_4(\text{OH})_2]$ .

### VIII.2.2.4 $\text{Sn}(\text{OH})\text{Cl}_3 \cdot 3\text{H}_2\text{O}(\text{s})$

The compound crystallises from concentrated aqueous solutions during drying above  $\text{CaCl}_2$  [1914PFE/MUL].

**VIII.2.2.5 Sn(OH)<sub>2</sub>Cl<sub>2</sub>(s)**

A solubility product  $K = 5 \times 10^{-56}$  is given by Kovalenko [1958KOV], derived from polarographic measurements in dilute hydrochloric acid. No reaction was formulated for the definition of  $K$ .

**VIII.2.2.6 Sn(OH)<sub>3</sub>Cl·H<sub>2</sub>O(s)**

This has been prepared in impure form only [1953MEU/LOS].

**VIII.2.3 Solubility of tin bromides****VIII.2.3.1 SnBr<sub>2</sub>(s)**

In pure water precipitation of hydroxide bromide occurs [1927BRE]. From solutions with high concentrations of HBr (1 to 6 mol·kg<sup>-1</sup> H<sub>2</sub>O) SnBr<sub>2</sub> can be extracted with ether in form of SnBr<sub>3</sub><sup>-</sup> [1962WOO/TAY] with a distribution coefficient of about 5 [1953BOC/KUS].

**VIII.2.3.2 SnBrF(s) and Sn<sub>3</sub>BrF<sub>5</sub>(s)**

The compounds crystallise from concentrated aqueous solutions containing HBr and are structurally well characterised [1969DON/SEN], [1972DON/PUX].

**VIII.2.3.3 SnBr<sub>4</sub>(s)****VIII.2.3.4 Hydrates of SnBr<sub>4</sub>**

From aqueous solutions SnBr<sub>4</sub>·4H<sub>2</sub>O can be crystallised [1884RAY/PRE], [1911MUL]. From an investigation of the melting diagram of the system SnBr<sub>4</sub>-H<sub>2</sub>O the compound SnBr<sub>4</sub>·8H<sub>2</sub>O ( $t_{\text{fus}} = 19\text{ }^{\circ}\text{C}$ ) was found to crystallise as transparent crystals at compositions of 66.7–73.6% SnBr<sub>4</sub> [1895PIC]. Wagman *et al.* [1968WAG/EVA] estimated a standard formation enthalpy of the octahydrate  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnBr}_4 \cdot 8\text{H}_2\text{O}, \text{s}, 298.15\text{ K}) = -661.5\text{ kcal}\cdot\text{mol}^{-1}$  (*i.e.*  $-2767.7\text{ kJ}\cdot\text{mol}^{-1}$ ).

**VIII.2.3.5 Sn(OH)Br<sub>3</sub>·3H<sub>2</sub>O(s)**

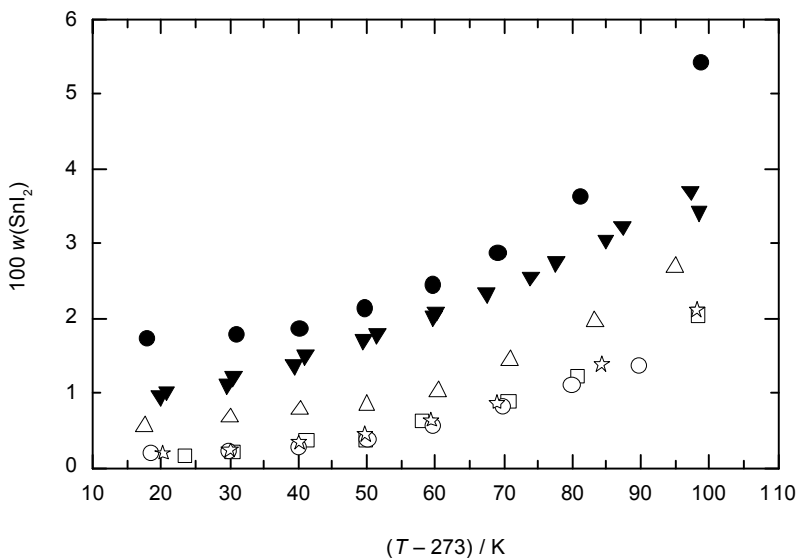
Only information concerning preparation is available [1905PFE], [1914PFE/MUL].

## VIII.2.4 Solubility of tin iodides

### VIII.2.4.1 $\text{SnI}_2(\text{s})$

Young [1897YOU] determined solubilities in the system  $\text{SnI}_2\text{-HI-H}_2\text{O}$  in a temperature range from 273 to 373 K. At constant temperature, the solubility of  $\text{SnI}_2$  decreases first by addition of HI up to about  $w(\text{HI}) \approx 0.1$ . With further addition of HI, it increases strongly.

Figure VIII-13: Solubility in the system  $\text{SnI}_2\text{-HI-H}_2\text{O}$  as a function of temperature and for different hydroiodic acid concentrations according to [1897YOU]. Experimental data:  $\blacktriangledown$ : pure water;  $\square$ :  $w(\text{HI}) = 5.83\%$ ;  $\circ$ :  $w(\text{HI}) = 9.50\%$ ;  $\star$ :  $w(\text{HI}) = 10.60\%$ ;  $\triangle$ :  $w(\text{HI}) = 15.20\%$ ;  $\bullet$ :  $w(\text{HI}) = 20.44\%$ .



Combining the recommended formation enthalpy and entropy data of  $\text{SnI}_2(\text{cr})$  a Gibbs energy of formation of  $\Delta_f G_m^\circ(\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = -160.528 \text{ kJ}\cdot\text{mol}^{-1}$  is derived. With an  $\alpha(\text{H}^+, \Gamma) = 0.195$  obtained from a SIT treatment of activity data in the system  $\text{HI-H}_2\text{O}$  at 25 °C [1959ROB/STO] and including the complex formation constants  $[\text{SnI}_q]^{2-q}$  for  $q = 1$  to 4 (see Section VIII.3.4.1) the solubility of tin(II) iodide can be calculated as a function of HI concentration. Figure VIII-15 shows the comparison with experimental data [1897YOU]. Good agreement gives evidence that the formation data derived from thermochemical measurements in the anhydrous system are consistent with aqueous solubility data.



Figure VIII-14: Solubility in the system  $\text{SnI}_2\text{-HI-H}_2\text{O}$  as a function of temperature and for higher hydroiodic acid concentrations according to [1897YOU]. Experimental data:  $\square$ :  $w(\text{HI}) = 24.88\%$ ;  $\circ$ :  $w(\text{HI}) = 30.40\%$ ;  $\star$ :  $w(\text{HI}) = 36.82\%$ .

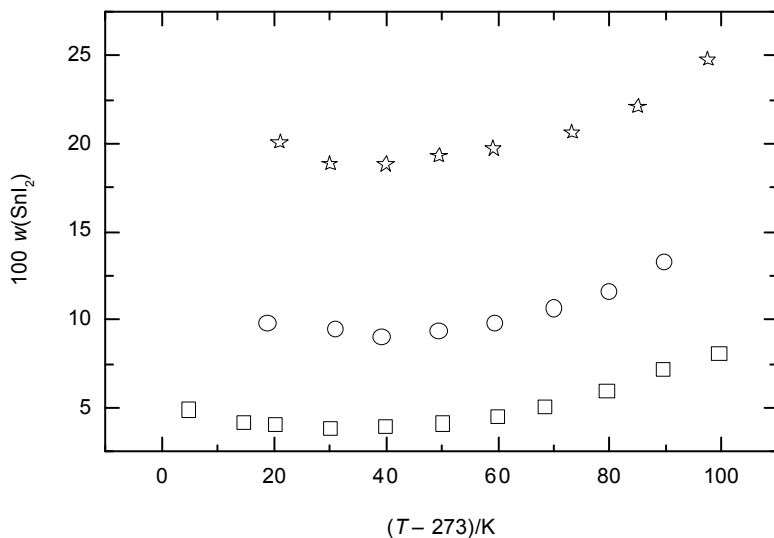
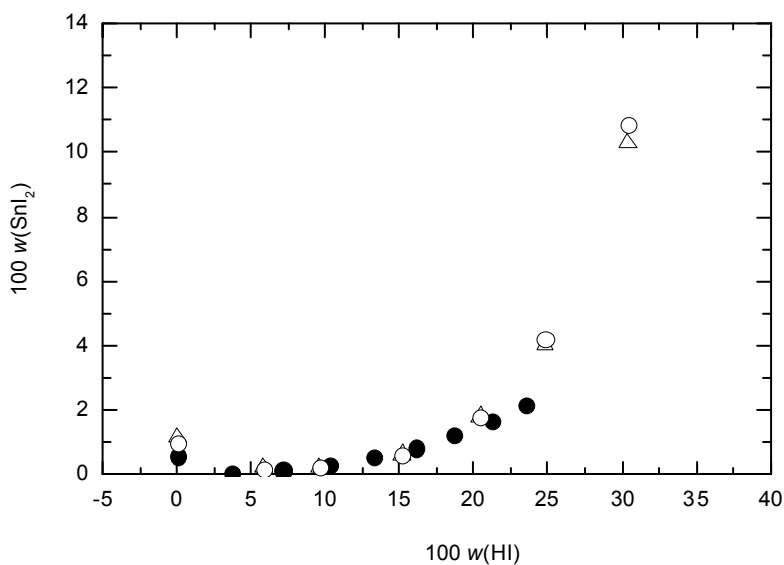


Figure VIII-15: Solubility of  $\text{SnI}_2(\text{cr})$  as a function of iodic acid concentration after [1897YOU] ( $\circ$ : experimental data at 20 °C;  $\triangle$ : experimental data at 30 °C;  $\bullet$ : calculated solubility at 25 °C).



### VIII.3 Aqueous halide complexes

Although a number of investigations have been published dealing with the halide complexes of tin(II) and tin(IV), relatively few spectroscopic data are available for these species in aqueous solutions.  $^{19}\text{F}$  and  $^{119}\text{Sn}$  NMR studies indicated the formation of three  $\text{SnI}_q^{2-q}$  species ( $q = 1$  to 3) [1959CON/POU], [1990KOK/RAK]. In the aqueous solutions of  $\text{SnX}_2 + \text{HX}$  ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) several species (probably  $\text{SnI}_q^{2-q}$ ,  $q = 1$  to 4) are in rapid equilibrium. When a mixture of hydrogen-halogenides were used, all the ten trihalogenostannate(II) anions ( $[\text{Sn}(\text{Cl}_x\text{Br}_y\text{I}_z)]^-$ ,  $x + y + z = 3$ ) have been identified by  $^{119}\text{Sn}$  NMR in the diethylether extract [1989COD/TAY]. A recent EXAFS study of tin(II) chloride solutions revealed the presence of the complexes  $\text{SnCl}_3^-$  and  $\text{SnCl}_4^{2-}$  at chloride concentrations between 0.5 and 2.5 M [2000SHE/RAG]. The relative stability of the tetrachlorido species increased with the temperature. Mössbauer spectroscopic studies conducted on a series of frozen aqueous solutions of tin(II) are also in favour of the presence of  $\text{SnX}_3^-$  ( $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-$ ) anions [1981CHE/HSU], [1984CHE/HSU], [1984HSU/CHE]. The  $\text{SnX}_3^-$  anions are pyramidal due to the presence of a sterically active nonbonding pair of electrons. This electron pair makes the  $\text{SnX}_3^-$  anions ( $\text{X} = \text{Cl}^-, \text{Br}^-$ ) excellent ligands, resulting in a wide range of metal-metal bounded transition metal complexes, such as  $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$  [1964YOU/GIL], [1984PRE/RUE].

Tin(IV) has strong hydrolyzing tendency, even in 1 M HX solution partially hydrolyzed halogeno complexes ( $\text{SnX}_y(\text{OH})_{6-y}^{2-y}$ ) may be present, which is often disregarded by the researcher. This is especially true in case of the NMR measurements, since the aqua and hydroxido complexes (e.g.  $\text{SnX}_3(\text{H}_2\text{O})_3^+$ ,  $\text{SnX}_3(\text{H}_2\text{O})_2\text{OH}(\text{aq})$ ,  $\text{SnX}_3(\text{H}_2\text{O})(\text{OH})_2^-$  and  $\text{SnX}_3(\text{OH})_3^{2-}$ ) are indistinguishable due to the fast proton exchange. Using varied concentrations of the halide ions the presence of all  $[\text{SnX}_{6-n}(\text{H}_2\text{O})_n]^{n-2}$  complexes ( $n = 0$  to 6,  $\text{X} = \text{Cl}^-$  and  $\text{Br}^-$ ) have been identified by  $^{119}\text{Sn}$  NMR spectroscopy, including the *cis/trans* and *fac/mer* isomers [1989MAO/YOU], [1989MAO/YOU2], [1992TAY/COD]. Mixtures of  $\text{SnCl}_4$  and  $\text{SnBr}_4$  in aqueous solution give rise to practically all possible aquohalostannate(IV) species with the composition of  $[\text{SnCl}_x\text{Br}_y(\text{H}_2\text{O})_z]^{z-2}$  (where  $x + y + z = 6$ ) [1992TAY/COD]. An EXAFS study indicated, that in solution containing 0.11 M HCl and 2.0 M NaCl, aqueous tin(IV) occurs exclusively as the  $\text{SnCl}_6^{2-}$  complex between 25 and 250 °C [2000SHE/RAG]. Mössbauer spectroscopic investigations reflected the stepwise formation of the  $[\text{SnX}_6]^{2-}$  ( $\text{X} = \text{F}^-, \text{Cl}^-$ ) complexes [1981CHE], [1981CHE2], [1991KHR/ZAP].

#### VIII.3.1 Aqueous fluoride complexes

##### VIII.3.1.1 Aqueous Sn(II) fluorides

Polarographic [1954SCH/DAV], [1970BON/TAY], [1990BEA/MEN], potentiometric measurements, using tin amalgam [1961CON/PAU], [1968HAL/SLA] and/or fluoride

selective electrode [1968HAL/SLA], [1975NEL/AMI], [1976SCH/CRO], [1985DJO/ZMB], and Mössbauer spectroscopic studies have been performed to establish the complex formation between tin(II) and fluoride ion. These investigations indicated the formation of the mononuclear  $\text{SnF}^+$ ,  $\text{SnF}_2(\text{aq})$  and  $\text{SnF}_3^-$  species with rather high stability. Complexes with higher coordination number ( $\text{SnF}_q^{2-q}$  with  $q > 3$ ) were not detected, not even in presence of 4000-fold excess of fluoride over tin(II) [1954SCH/DAV]. In more concentrated tin(II) solutions than used in the above studies ( $[\text{Sn}^{2+}] > 0.3 \text{ M}$ ,  $[\text{F}^-] > 0.6 \text{ M}$ ) the formation of a dinuclear  $\text{Sn}_2\text{F}_5^-$  complex with a bridging fluoride ion was also reported [1964DON/DON], but equilibrium data are not available for this species. The reported and recalculated formation constants of the mononuclear complexes are listed in Table VIII-7. The formation constants given in [1985DJO/ZMB] determined at 295.15 K have been included as reported, since the temperature correction to 298.15 K is assumed to be negligible.

Table VIII-7: Experimental formation constants of the species  $\text{SnF}_q^{2-q}$ .

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{F}^- \rightleftharpoons \text{SnF}^+$						
ise-F	1 M $\text{NaClO}_4$	25	4.08	$4.55 \pm 0.15$	$4.53 \pm 0.30$	[1970BON/TAY]
ise-F	3 M $\text{NaClO}_4$	25	4.58		$4.52 \pm 0.20$	[1976SCH/CRO]
ise-F	0.1 M $\text{NaClO}_4$	23	4.78		$4.77 \pm 0.30$	[1985DJO/ZMB]
			4.61		$4.60 \pm 0.30$	
			4.58		$4.55 \pm 0.30$	
ise-Sn	0.5 M (H/Na) $\text{ClO}_4$	25	4.14			[1961CON/PAU]
			4.06			
ise-F,Sn	0.8 M	25	6.26	$4.60 \pm 0.24$		[1968HAL/SLA]
			45	5.78	$4.62 \pm 0.15$	
			60	6.21	$4.72 \pm 0.12$	
ise-F	0.0333 M $\text{Na}_2\text{SO}_4$	25	3.60			[1975NEL/AMI]
Möss <sup>(c)</sup>	0.65 M $\text{HClO}_4$	<sup>(d)</sup>	4.5			[1981CHE/HSU]
pol	2 – 100 w% HF	25	6.5			[1990BEA/MEN]
$\text{Sn}^{2+} + 2 \text{F}^- \rightleftharpoons \text{SnF}_2(\text{aq})$						
ise-F	3 M $\text{NaClO}_4$	25	8.34		$8.21 \pm 0.20$	[1976SCH/CRO]
ise-F	0.1 M $\text{NaClO}_4$	22	8.26		$8.25 \pm 0.30$	[1985DJO/ZMB]
			8.01		$7.99 \pm 0.30$	
			7.94		$7.90 \pm 0.30$	
pol	0.8 M $\text{NaNO}_3$	25	–	$7.91 \pm 0.30$	$7.89 \pm 0.30$	[1954SCH/DAV]

(Continued on next page)

Table VIII-7 (continued)

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
ise-F,Sn	0.8 M ?	25	8.76	$8.01 \pm 0.24$		[1968HAL/SLA]
		45	8.70	$7.92 \pm 0.21$		
		60	9.06	$8.73 \pm 0.09$		
ise-F	1 M NaClO <sub>4</sub>	25	6.68	$6.8 \pm 1.0$		[1970BON/TAY]
ise-F	0.0333 M Na <sub>2</sub> SO <sub>4</sub>	25	7.04			[1975NEL/AMI]
Möss <sup>(c)</sup>	0.65 M HClO <sub>4</sub>	<sup>(d)</sup>	7.9			[1981CHE/HSU]
pol	2 – 100 w% HF	25	16.0			[1990BEA/MEN]
<b>Sn<sup>2+</sup> + 3 F<sup>-</sup> ⇌ SnF<sub>3</sub><sup>-</sup></b>						
ise-F	1 M NaClO <sub>4</sub>	25	9.46	$9.43 \pm 0.10$	$9.37 \pm 0.30$	[1970BON/TAY]
ise-F	3 M NaClO <sub>4</sub>	25	11.32		$11.12 \pm 0.20$	[1976SCH/CRO]
ise-F	0.1 M NaClO <sub>4</sub>	22	12.24		$12.23 \pm 2.00$	[1985DJO/ZMB]
			11.97		$11.94 \pm 2.00$	
			11.80		$11.73 \pm 2.00$	
pol	0.8 M NaNO <sub>3</sub>	25	9.92	$9.78 \pm 0.30$	$9.74 \pm 0.30$	[1954SCH/DAV]
			10.96	$10.76 \pm 0.30$	$10.65 \pm 0.30$	
ise-F,Sn	0.8 M ?	25	9.25	$10.38 \pm 0.18$		[1968HAL/SLA]
		45	9.82	$10.40 \pm 0.12$		
		60	10.31	$10.47 \pm 0.27$		
ise-F	0.0333 M Na <sub>2</sub> SO <sub>4</sub>	25	9.00			[1975NEL/AMI]
Möss <sup>(c)</sup>	0.65 M HClO <sub>4</sub>	<sup>(d)</sup>	10.4			[1981CHE/HSU]

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

(c) Mössbauer spectroscopy

(d) Equilibrated at room temperature than measured in a fast-frozen solution

The SIT analysis of the accepted formation constants for Reaction ((VIII.9),  $q = 1$ ) is depicted in Figure VIII-16.

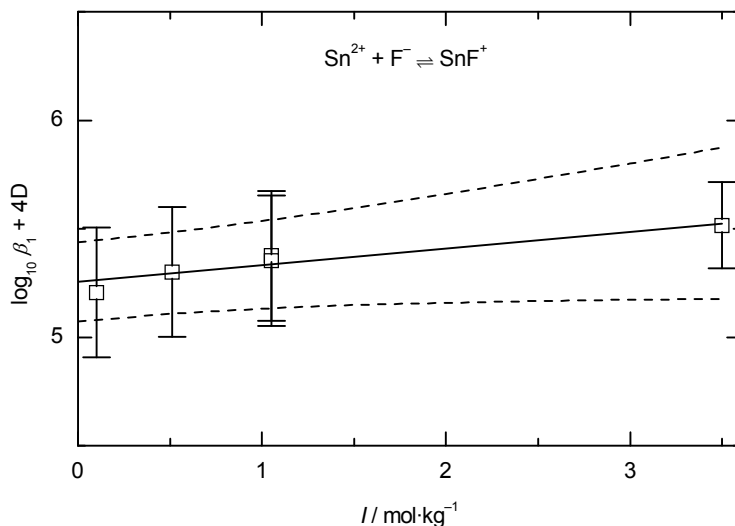


The weighted linear regression using 5 data points yielded the selected value of:

$$\log_{10} \beta_1^0 ((\text{VIII.9}), q = 1, 298.15 \text{ K}) = (5.25 \pm 0.19).$$

The corresponding value of  $\Delta \mathcal{A}(\text{VIII.9}), q = 1$  is  $-(0.08 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ . Using the selected values for  $\mathcal{A}(\text{Sn}^{2+}, \text{ClO}_4^-)$  and  $\mathcal{A}(\text{Na}^+, \text{F}^-)$ ,  $\Delta \mathcal{A}(\text{VIII.9}), q = 1$  leads to a value of  $\mathcal{A}(\text{SnF}^+, \text{ClO}_4^-) = (0.14 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ .

Figure VIII-16: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{F}^- \rightleftharpoons \text{SnF}^+$  in  $\text{NaClO}_4$  media ( $\square$ : experimental data from: [1985DJO/ZMB], [1976SCH/CRO] and [1970BON/TAY]).



A similar treatment (*cf.* Figure VIII-17) of the accepted data for Reaction ((VIII.9),  $q = 2$ ) resulted in the selected value of

$$\log_{10} \beta_2^{\circ} ((\text{VIII.9}), q = 2, 298.15 \text{ K}) = (8.89 \pm 0.21).$$

From the slope in Figure VIII-17,  $\Delta \alpha((\text{VIII.9}), q = 2) = -(0.23 \pm 0.09) \text{ kg} \cdot \text{mol}^{-1}$  and  $\alpha(\text{SnF}_{2+}(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.01 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$  ( $\approx 0.00 \text{ kg} \cdot \text{mol}^{-1}$ ) can be derived.

Although there is no doubt concerning the formation of the trifluoro species, the  $\log_{10} \beta_3$  values reported in [1970BON/TAY] and [1985DJO/ZMB] for  $\text{NaClO}_4$  media are rather scattered (Figure VIII-18). Since the experiments of the above papers seem to be equally reliable, the inherent uncertainties of the reported/re-evaluated constants were considerably increased (see Appendix A). The SIT treatment of the five available experimental data for  $\text{NaClO}_4$  media resulted in

$$\log_{10} \beta_3^{\circ} ((\text{VIII.9}), q = 3, 298.15 \text{ K}) = (11.5 \pm 1.0).$$

Figure VIII-17: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 2\text{F}^- \rightleftharpoons \text{SnF}_2(\text{aq})$  in  $\text{NaClO}_4$  media ( $\square$ : experimental data from [1985DJO/ZMB], [1976SCH/CRO] and [1970BON/TAY];  $*$ : experimental data from [1954SCH/DAV] not included in the SIT analysis).

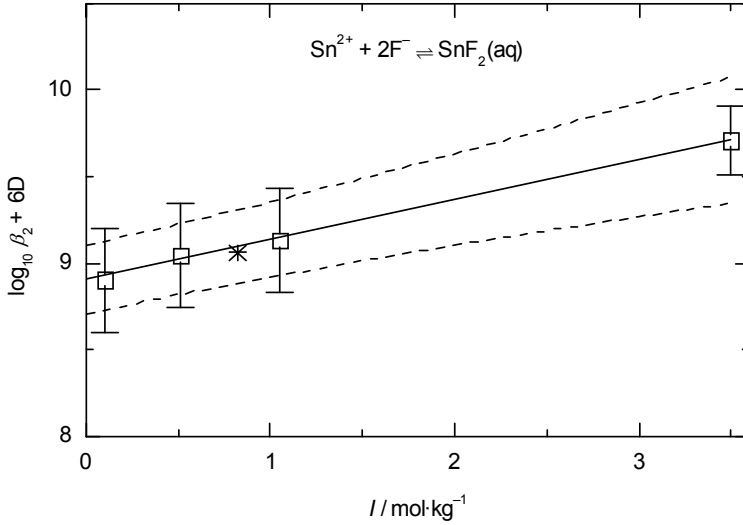
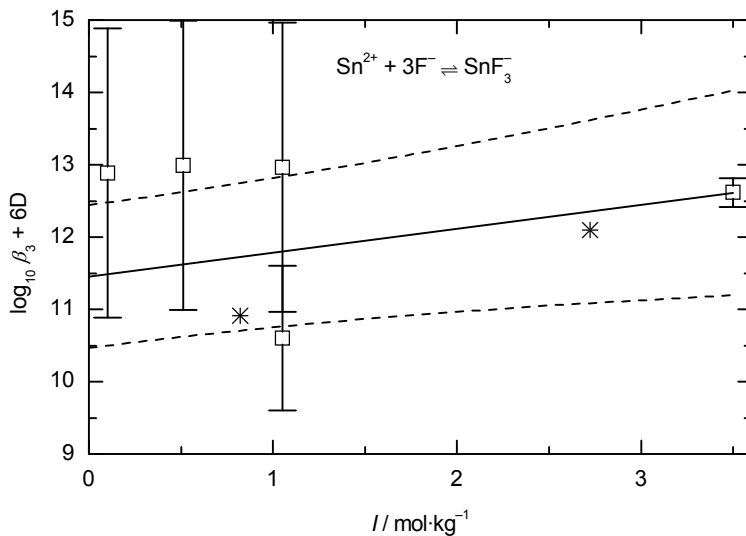


Figure VIII-18: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 3\text{F}^- \rightleftharpoons \text{SnF}_3^-$  in  $\text{NaClO}_4$  media ( $\square$ : experimental data from [1985DJO/ZMB], [1976SCH/CRO] and [1970BON/TAY];  $*$ : experimental data from [1954SCH/DAV] not included in the SIT analysis).



The above listed selected thermodynamic formation constants correspond to

$$\Delta_f G_m^\circ (\text{(VIII.9)}, q = 1, 298.15 \text{ K}) = - (30.0 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{(VIII.9)}, q = 2, 298.15 \text{ K}) = - (50.7 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{(VIII.9)}, q = 3, 298.15 \text{ K}) = - (65.6 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1},$$

and hence

$$\Delta_f G_m^\circ (\text{SnF}^+, \text{aq}, 298.15 \text{ K}) = - (338.9 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{SnF}_2, \text{aq}, 298.15 \text{ K}) = - (641.2 \pm 1.9) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{SnF}_3^-, \text{aq}, 298.15 \text{ K}) = - (937.6 \pm 6.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

### VIII.3.1.2 Aqueous Sn(IV) fluorides

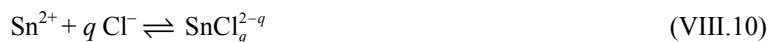
Tin(IV) forms very stable complexes with fluoride ion. Three papers report equilibrium data for the binary tin(IV)-fluoride system, but neither of them are suitable to derive selected values. The Mössbauer spectroscopic study reported in [1981CHE] is not considered in this review (see Appendix A).  $^{19}\text{F}$  NMR data were used to calculate  $\log_{10} K_6 \approx 5.6$  for the reaction  $\text{SnF}_5(\text{H}_2\text{O})^- + \text{F}^- \rightleftharpoons \text{SnF}_6^{2-} + \text{H}_2\text{O}(\text{l})$  at 22 °C and at high ionic strength ( $I \approx 4.2 \text{ M}$ ) [1968DEA/EVA]. Based on their polarographic data Schaap *et al.* estimated  $\log_{10} \beta_6 \approx 25$  ( $I = 0.1$  to  $0.2 \text{ M}$ ,  $0.1 \text{ M KF} + 0$  to  $0.1 \text{ M HF}$ ) for the reaction  $\text{Sn}^{4+} + 6 \text{F}^- \rightleftharpoons \text{SnF}_6^{2-}$  [1954SCH/DAV]. The latter value can be used as a rough estimate.

## VIII.3.2 Aqueous chloride complexes

### VIII.3.2.1 Aqueous Sn(II) chlorides

The complex formation between tin(II) and chloride ion has been studied by solubility [1962HAI/ZOL], spectrophotometric [2001MUL/SEW], polarographic [1949RIC/POP], voltammetric [1981PET/MIL], kinetic [1951DUK/PIN], electrophoretic [1969CAR] and potentiometric [1928PRY], [1950DUK/COU], [1952VAN/RHO], [1961TOB/HUG], [1975FED/BOL], [1976SAM/LYA] methods. Most of these papers report the formation of the species  $\text{SnCl}_q^{2-q}$  ( $q = 1$  to  $3$ ). The experimental work is well documented in [1928PRY], [1949RIC/POP], [1950DUK/COU], [1952VAN/RHO] and [1981PET/MIL] which allowed a re-evaluation of the data for the purposes of this review. For reasons mentioned in Appendix A, the data reported in [1949RIC/POP], [1962HAI/ZOL] and [1976SAM/LYA] were rejected in this review.

The reported and recalculated formation constants for the Reactions ((VIII.10),  $q = 1$  to  $4$ )



are listed in Table VIII-8. The formation constants determined in 6 M NaClO<sub>4</sub> solution were not considered in the SIT extrapolations, since the ionic strength ( $I = 8.912 \text{ mol}\cdot\text{kg}^{-1}$ ) is well above of the recommended range.

Table VIII-8: Experimental formation constants of the species  $\text{SnCl}_q^{2-q}$ .

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$						
Ise-Sn	0 corr ((H/K)Cl)	25	1.51	1.34	$1.34 \pm 0.50$	[1928PRY]
pol	0 corr (KCl)	?	1.85			[1949RIC/POP]
Ise-Sn	2.03 M HClO <sub>4</sub>	25	$1.05 \pm 0.01$	$1.07 \pm 0.20$	$1.03 \pm 0.40^c$	[1950DUK/COU]
kin	2.03 M HClO <sub>4</sub>	25	1.11		$1.07 \pm 0.50$	[1951DUK/PIN]
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	0.97	$0.96 \pm 0.02$	$0.89 \pm 0.30$	[1952VAN/RHO]
		25	1.15	$1.13 \pm 0.03$	$1.05 \pm 0.30$	
		35	1.22	$1.17 \pm 0.04$	$1.10 \pm 0.30$	
		45	1.27	$1.23 \pm 0.03$	$1.15 \pm 0.30$	
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	25	$1.18 \pm 0.01$		$1.11 \pm 0.20$	[1961TOB/HUG]
sol	4 M H <sub>2</sub> SO <sub>4</sub> /HCl	25	1.45			[1962HAI/ZOL]
em	HCl (varied)	25	1.05			[1969CAR]
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	1.09		$1.08 \pm 0.40$	[1975FED/BOL]
	1.0 M NaClO <sub>4</sub>	25	1.02		$1.00 \pm 0.40$	
	3.0 M NaClO <sub>4</sub>	25	1.18		$1.11 \pm 0.40$	
	4.0 M NaClO <sub>4</sub>	25	1.34		$1.25 \pm 0.40$	
	6.0 M NaClO <sub>4</sub>	25	1.80		$1.63 \pm 0.40$	
Ise-Sn	1.0 M LiClO <sub>4</sub>	25	1.08			[1976SAM/LYA]
vlt	1.0 M NaNO <sub>3</sub>	20	$0.73 \pm 0.10$	$0.66 \pm 0.11$		[1981PET/MIL]
	0 corr (NaCl)	20		$1.25 \pm 0.50$	$1.25 \pm 0.50$	
Möss <sup>(d)</sup>	3.5 M (Na,H)(ClO <sub>4</sub> ,Cl)	<sup>(e)</sup>	1.18			[1984CHE/HSU]
spe	0 corr ((H/Na)Cl)	25	$1.42 \pm 0.05$		$1.42 \pm 0.30$	[2001MUL/SEW] <sup>(f)</sup>
		50	$1.45 \pm 0.08$		$1.45 \pm 0.30$	
		100	$1.43 \pm 0.10$		$1.43 \pm 0.40$	
		150	$1.52 \pm 0.04$		$1.52 \pm 0.40$	
		200	$1.58 \pm 0.08$		$1.58 \pm 0.40$	
$\text{Sn}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{SnCl}_2(\text{aq})$						
Ise-Sn	0 corr ((H/K)Cl)	25	2.25	2.13	$2.13 \pm 0.50$	[1928PRY]
pol	0 corr (KCl)	?	2.31			[1949RIC/POP]
Ise-Sn	2.03 M HClO <sub>4</sub>	25	$1.76 \pm 0.02$	$1.6 \pm 0.4$		[1950DUK/COU]

(Continued on next page)



Table VIII-8 (continued)

Method	Ionic media	<i>t</i> /°C	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	1.53	1.46 ± 0.04	1.32 ± 0.30	[1952VAN/RHO]
		25	1.70	1.67 ± 0.07	1.54 ± 0.30	
		35	1.78	1.78 ± 0.10	1.64 ± 0.30	
		45	1.86	1.83 ± 0.09	1.70 ± 0.30	
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	25	1.74 ± 0.02		1.61 ± 0.20	[1961TOB/HUG]
sol	4 M H <sub>2</sub> SO <sub>4</sub> /HCl	25	2.35			[1962HAI/ZOL]
em	HCl (varied)	25	1.71			[1969CAR]
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	1.36		1.34 ± 0.40	[1975FED/BOL]
	1.0 M NaClO <sub>4</sub>	25	1.13		1.09 ± 0.40	
	3.0 M NaClO <sub>4</sub>	25	1.78		1.65 ± 0.40	
	4.0 M NaClO <sub>4</sub>	25	2.12		1.93 ± 0.40	
	6.0 M NaClO <sub>4</sub>	25	3.04		2.70 ± 0.40	
Ise-Sn	1.0 M LiClO <sub>4</sub>	25	1.85			[1976SAM/LYA]
vlt	1.0 M NaNO <sub>3</sub>	20	1.08 ± 0.10	1.12 ± 0.07		[1981PET/MIL]
	0 corr (NaCl)	20		1.99 ± 0.50	1.99 ± 0.50	
Möss <sup>(d)</sup>	3.5 M (Na,H)(ClO <sub>4</sub> ,Cl)	<sup>(e)</sup>	1.95			[1984CHE/HSU]
spe	0 corr ((H/Na)Cl)	25	2.18 ± 0.03		2.18 ± 0.30	[2001MUL/SEW] <sup>(f)</sup>
		50	2.25 ± 0.08		2.25 ± 0.30	
		100	2.25 ± 0.08		2.25 ± 0.40	
		150	2.52 ± 0.09		2.52 ± 0.40	
		200	2.83 ± 0.06		2.83 ± 0.40	
		250	3.06 ± 0.05		3.06 ± 0.50	
		300	3.56 ± 0.05		3.56 ± 0.50	
$\text{Sn}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{SnCl}_3^-$						
Ise-Sn	0 corr ((H/K)Cl)	25	2.02	1.99	1.99 ± 0.50	[1928PRY]
pol	0 corr (KCl)	?	1.94			[1949RIC/POP]
Ise-Sn	2.03 M HClO <sub>4</sub>	25	1.14 ± 0.13			[1950DUK/COU]
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	1.36	1.39 ± 0.08	1.19 ± 0.30	[1952VAN/RHO]
		25	1.68	1.59 ± 0.16	1.39 ± 0.30	
		35	1.83	1.67 ± 0.24	1.47 ± 0.30	
		45	1.95	1.90 ± 0.14	1.70 ± 0.30	
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	25	1.67 ± 0.04		1.48 ± 0.20	[1961TOB/HUG]
sol	4 M H <sub>2</sub> SO <sub>4</sub> /HCl	25	2.46			[1962HAI/ZOL]
em	HCl (varied)	25	1.69			[1969CAR]

(Continued on next page)

Table VIII-8 (continued)

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	1.65		1.45 ± 0.40	[1975FED/BOL]
	4.0 M NaClO <sub>4</sub>	25	2.12		1.84 ± 0.40	
	6.0 M NaClO <sub>4</sub>	25	3.30		2.78 ± 0.40	
vlt	0 corr (NaCl)	20		1.94 ± 0.50	1.94 ± 0.50	[1981PET/MIL]
Möss <sup>(d)</sup>	3.5 M (Na,H)(ClO <sub>4</sub> ,Cl)	<sup>(e)</sup> 1.78				[1984CHE/HSU]
spe	0 corr ((H/Na)Cl)	25	2.33 ± 0.04		2.33 ± 0.30	[2001MUL/SEW] <sup>(f)</sup>
		50	2.21 ± 0.09		2.21 ± 0.30	
		100	2.39 ± 0.06		2.39 ± 0.40	
		150	2.59 ± 0.10		2.59 ± 0.40	
		200	3.13 ± 0.04		3.13 ± 0.40	
		250	3.96 ± 0.04		3.96 ± 0.50	
		300	4.66 ± 0.03		4.66 ± 0.50	
<hr/> $\text{Sn}^{2+} + 4 \text{Cl}^- \rightleftharpoons \text{SnCl}_4^{2-}$ <hr/>						
Ise-Sn	0 corr ((H/K)Cl)	25	1.50			[1928PRY]
pol	0 corr (KCl)	?	2.00			[1949RIC/POP]
Ise-Sn	2.03 M HClO <sub>4</sub>	25	1.14 ± 0.35			[1950DUK/COU]
sol	4 M H <sub>2</sub> SO <sub>4</sub> /HCl	25	2.31			[1962HAI/ZOL]
spe	0 corr ((H/Na)Cl)	25	2.03 ± 0.02		2.03 ± 0.30	[2001MUL/SEW] <sup>(f)</sup>
		50	1.98 ± 0.10		1.98 ± 0.30	
		100	1.95 ± 0.10		1.95 ± 0.40	
		150	1.97 ± 0.14		1.97 ± 0.40	

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

(c) Corrected to NaClO<sub>4</sub> medium.

(d) Mössbauer spectroscopy.

(e) Equilibrated at room temperature, then measured in a fast-frozen solution.

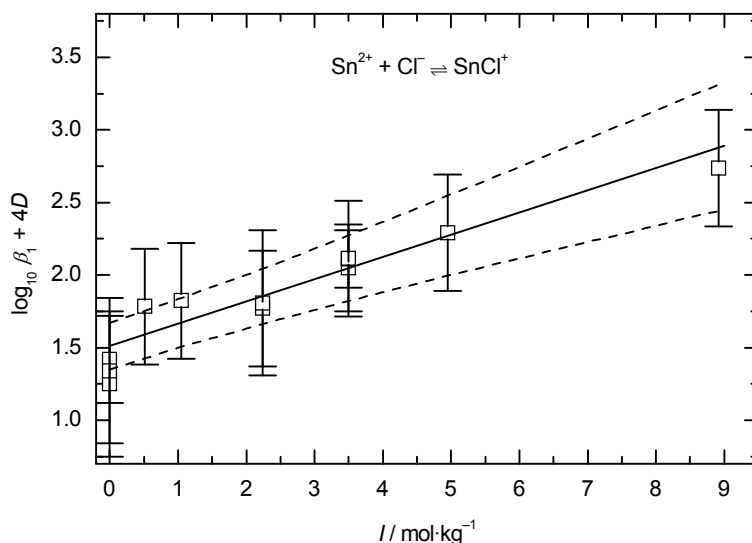
(f) Measured at the equilibrium saturated vapor pressure of the system.

The weighted linear regression of the remaining ten data points available for the formation of SnCl<sup>+</sup> in perchlorate media at 25 °C (Figure VIII-19), resulted in the following selected values:

$$\log_{10} \beta_1^\circ ((\text{VIII.10}), q = 1, 298.15 \text{ K}) = (1.52 \pm 0.20)$$

and  $\Delta\alpha(\text{VIII.10}, q = 1) = -(0.15 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ . Using the latter value,  $\alpha(\text{Sn}^{2+}, \text{ClO}_4^-)$  and  $\alpha(\text{Na}^+, \text{Cl}^-)$ , the ion interaction coefficient  $\alpha(\text{SnCl}^+, \text{ClO}_4^-) = (0.08 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$  is calculated.

Figure VIII-19: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$  in  $\text{NaClO}_4$  media. Experimental data from: [1928PRY], [1950DUK/COU], [1951DUK/PIN], [1952VAN/RHO], [1961TOB/HUG], [1975FED/BOL] and [2001MUL/SEW].



A similar treatment (Figure VIII-20 and Figure VIII-21) of the accepted data for the Reactions ((VIII.10),  $q = 2$  and 3) resulted in the selected values:

$$\log_{10} \beta_2^0 ((\text{VIII.10}), q = 2, 298.15 \text{ K}) = (2.17 \pm 0.17)$$

and

$$\log_{10} \beta_3^0 ((\text{VIII.10}), q = 3, 298.15 \text{ K}) = (2.13 \pm 0.19).$$

The slope of the straight lines in Figure VIII-20 and Figure VIII-21 correspond to  $\Delta\alpha(\text{VIII.10}, q = 2) = -(0.26 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  and  $\Delta\alpha(\text{VIII.10}, q = 3) = -(0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ , respectively. From these values  $\alpha(\text{SnCl}_2(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.00 \pm 0.007) \text{ kg}\cdot\text{mol}^{-1}$  and  $\alpha(\text{Na}^+, \text{SnCl}_3^-) = (0.04 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$  can be derived.

Figure VIII-20: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{SnCl}_2(\text{aq})$  in  $\text{NaClO}_4$  media. Experimental data from: [1928PRY], [1952VAN/RHO], [1961TOB/HUG], [1975FED/BOL] and [2001MUL/SEW].

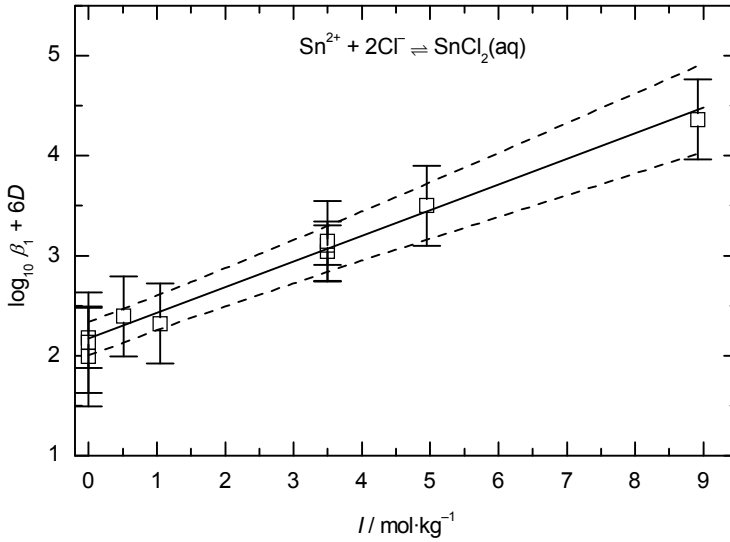
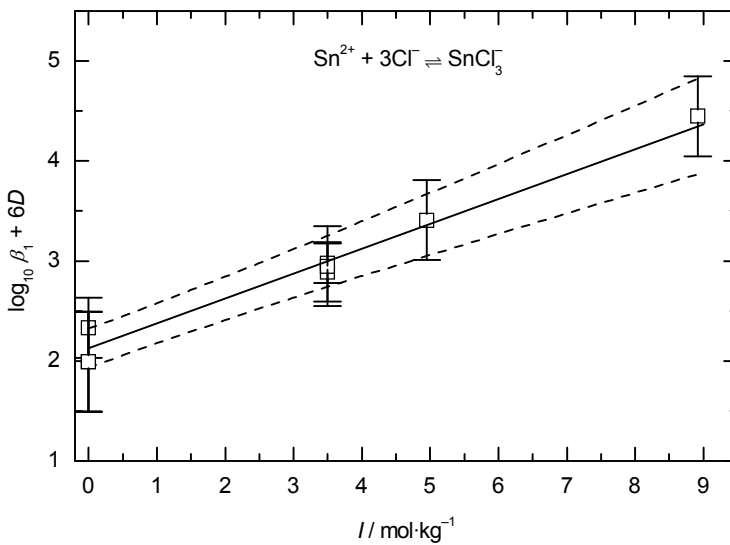


Figure VIII-21: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{SnCl}_3^-$  in  $\text{NaClO}_4$  media. Experimental data from: [1928PRY], [1952VAN/RHO], [1961TOB/HUG], [1975FED/BOL] and [2001MUL/SEW].



Beside the above mentioned complexes, the presence of the species  $\text{SnCl}_4^{2-}$  has been also suggested in [1928PRY], [1949RIC/POP], [1950DUK/COU], [1962HAI/ZOL] and [2001MUL/SEW]. The SIT treatment of the data in [1928PRY] indicated the formation of only three complexes ( $\text{SnCl}_q^{2-q}$ ,  $q = 1$  to 3). A similar conclusion can be drawn from the data in [1950DUK/COU] (see Appendix A), in agreement with the earlier recalculations described in [1961RAB/MOO] and [1961TOB/HUG]. The data reported in [1949RIC/POP] and [1962HAI/ZOL] were excluded from the selection procedure, due to the inappropriate experimental conditions used (see Appendix A). Nevertheless, the presence of the 1:4 complex at sufficiently high chloride concentrations, as used in [1949RIC/POP], [1962HAI/ZOL] and [2001MUL/SEW], is very likely, and its formation is further supported by the EXAFS study reported in [2000SHE/RAG]. Only a single reliable formation constant is available for the 1:4 complex, reported in [2001MUL/SEW]. Taking into account that the thermodynamic formation constants derived by these authors for the complexes  $\text{SnCl}_q^{2-q}$  ( $q = 1$  to 3) agree well with the values selected in this review (see Table VIII-8), the  $\log_{10} \beta_4^\circ$  value reported in [2001MUL/SEW] has been selected with somewhat increased uncertainty

$$\log_{10} \beta_4^\circ ((\text{VIII.10}), q = 4, 298.15 \text{ K}) = (2.03 \pm 0.40).$$

The selected thermodynamic formation constants, listed above, correspond to

$$\Delta_r G_m^\circ ((\text{VIII.10}), q = 1, 298.15 \text{ K}) = -(8.6 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ ((\text{VIII.10}), q = 2, 298.15 \text{ K}) = -(12.4 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ ((\text{VIII.10}), q = 3, 298.15 \text{ K}) = -(12.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ ((\text{VIII.10}), q = 4, 298.15 \text{ K}) = -(11.6 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1},$$

and hence

$$\Delta_r G_m^\circ (\text{SnCl}^+, \text{aq}, 298.15 \text{ K}) = -(167.20 \pm 0.96) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ (\text{SnCl}_2, \text{aq}, 298.15 \text{ K}) = -(302.22 \pm 1.07) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ (\text{SnCl}_3^-, \text{aq}, 298.15 \text{ K}) = -(433.24 \pm 1.19) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r G_m^\circ (\text{SnCl}_4^{2-}, \text{aq}, 298.15 \text{ K}) = -(563.86 \pm 2.37) \text{ kJ}\cdot\text{mol}^{-1}.$$

Only three publications [1952VAN/RHO], [1976VAS/KOK] and [2001MUL/SEW] reported enthalpy values for the Reactions ((VIII.10),  $q = 1$  to 3). The experimental data, together with the recalculated values, are collected in Table VIII-9. The influence of temperature on the formation constants was used to calculate the enthalpy values in [1952VAN/RHO] and [2001MUL/SEW]. However, the temperature variation of the  $\log_{10} \beta_q$  values is comparable with, or even smaller than, their uncertainties (Table VIII-8). Therefore, in the present review the calorimetric data reported by Vasil'ev *et al.* in [1973VAS/VAS] and [1976VAS/KOK] have been

re-evaluated to derive selected enthalpy values for the Reactions ((VIII.10),  $q = 1, 2$ ). The details of the re-evaluation are provided in Appendix A. The recalculated enthalpy values were extrapolated to zero ionic strength using the SIT model.

The weighted linear regression of the four data points measured in perchloric acid solutions at 25 °C (Figure VIII-22), resulted in

$$\Delta_r H_m^\circ((\text{VIII.10}), q = 1, 298.15 \text{ K}) = (12.7 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{and } \Delta \varepsilon_L((\text{VIII.10}), q = 1) = (1.9 \pm 1.0) \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}.$$

Table VIII-9: Experimental enthalpy values for Reactions ((VIII.10),  $q = 1$  to 3).

Method	Medium	$t/^\circ\text{C}$	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )		Reference
			Reported	Accepted	
<b>Sn<sup>2+</sup> + Cl<sup>-</sup> ⇌ SnCl<sup>+</sup></b>					
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0 – 45	10.9 ± 1.7	9.8 ± 2.0 <sup>(a)</sup>	[1952VAN/RHO]
cal	0 corr HClO <sub>4</sub>	15	6.8 ± 0.8		[1976VAS/KOK]/
	0 corr HClO <sub>4</sub>	25	9.2 ± 1.8		[1973VAS/VAS]
	0.20 M HClO <sub>4</sub>	15	5.7 ± 1.8		
	0.49 M HClO <sub>4</sub>	15	5.7 ± 1.0		
	0.49 M HClO <sub>4</sub>	25	7.9 ± 1.1		
	1.02 M HClO <sub>4</sub>	15	5.8 ± 0.9		
	1.02 M HClO <sub>4</sub>	25	7.7 ± 0.8	8.9 ± 2.4 <sup>(a)</sup>	
	1.96 M HClO <sub>4</sub>	15	5.5 ± 0.9		
	1.96 M HClO <sub>4</sub>	25	6.9 ± 0.8	7.0 ± 1.3 <sup>(a)</sup>	
	2.93 M HClO <sub>4</sub>	15	4.9 ± 1.1		
	2.93 M HClO <sub>4</sub>	25	6.3 ± 0.9	4.9 ± 1.8 <sup>(a)</sup>	
spe	0 corr ((H/Na)Cl)	25	0.10	3.1 ± 2.0 <sup>(a)</sup>	[2001MUL/SEW] <sup>(b)</sup>
		50	0.55		
		100	1.91		
		150	3.97		
		200	6.86		
<b>Sn<sup>2+</sup> + 2 Cl<sup>-</sup> ⇌ SnCl<sub>2</sub>(aq)</b>					
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0 – 45	13.4 ± 3.3	14.1 ± 2.0 <sup>(a)</sup>	[1952VAN/RHO]
cal	1.02 M HClO <sub>4</sub>	25		13.0 ± 5.7 <sup>(a)</sup>	[1976VAS/KOK]
	1.96 M HClO <sub>4</sub>	25		10.8 ± 2.7 <sup>(a)</sup>	
	2.93 M HClO <sub>4</sub>	25		9.1 ± 3.2 <sup>(a)</sup>	
	3.95 M HClO <sub>4</sub>	25		4.3 ± 3.0 <sup>(a)</sup>	

(Continued on next page)

Table VIII-9 (continued)

Method	Medium	$t/^\circ\text{C}$	$\Delta_r H_m$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )		Reference
			Reported	Accepted	
spe	0 corr ((H/Na)Cl)	25	1.01		[2001MUL/SEW] <sup>(b)</sup>
		50	2.75		
		100	7.86		
		150	15.47		
		200	25.96		
		250	40.2		
		300	58.1		
<hr/>					
$\text{Sn}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{SnCl}_3^-$					
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0 – 45	23.4 ± 6.3	17.2 ± 4.0 <sup>(a)</sup>	[1952VAN/RHO]
spe	0 corr ((H/Na)Cl)	25	-3.99		[2001MUL/SEW] <sup>(b)</sup>
		50	-0.80		
		100	10.06		
		150	26.87		
		200	50.96		
		250	83.9		
		300	126.3		

(a) Re-evaluated values, see Appendix A.

(b) Measured at the equilibrium saturated vapor pressure of the system.

The formation of  $\text{SnCl}_2(\text{aq})$  never exceeds 20% of the total tin(II) concentration under the conditions used for the calculation, thus the corresponding enthalpy values are somewhat less accurate. From the plot in Figure VIII-23

$$\Delta_r H_m^\circ((\text{VIII.10}), q = 2, 298.15 \text{ K}) = (19.7 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}$$

and  $\Delta \varepsilon_L((\text{VIII.10}), q = 2) = (2.9 \pm 1.8) \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$  can be derived.

The endothermic enthalpies reflect predominantly electrostatic interaction between tin(II) and chloride ion. The reaction enthalpies of the formation of  $\text{SnCl}^+$  and  $\text{SnCl}_2(\text{aq})$  obtained from the experimental data of Vanderzee and Rhodes [1952VAN/RHO] at  $I = 3 \text{ M}$  (Table VIII-9) are relatively close to those selected in this review. Although the standard reaction enthalpy for the Reaction ((VIII.10),  $q = 3$ ) cannot be selected, a tentative value of  $\Delta_r H_m^\circ((\text{VIII.10}), q = 3) = (17.4 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$ , derived from [1952VAN/RHO], can be used until more precise data will be published.

Figure VIII-22: Extrapolation to  $I = 0$  of the experimental enthalpy data for reaction  $\text{Sn}^{2+} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$  in  $\text{HClO}_4$  media.  $D_L = \frac{3}{4}A_L\sqrt{I_m}/(1+1.5\sqrt{I_m})$  see [2005HUM/AND] Eq. (V.58 pp. 99-100). Experimental data are recalculated from [1973VAS/VAS].

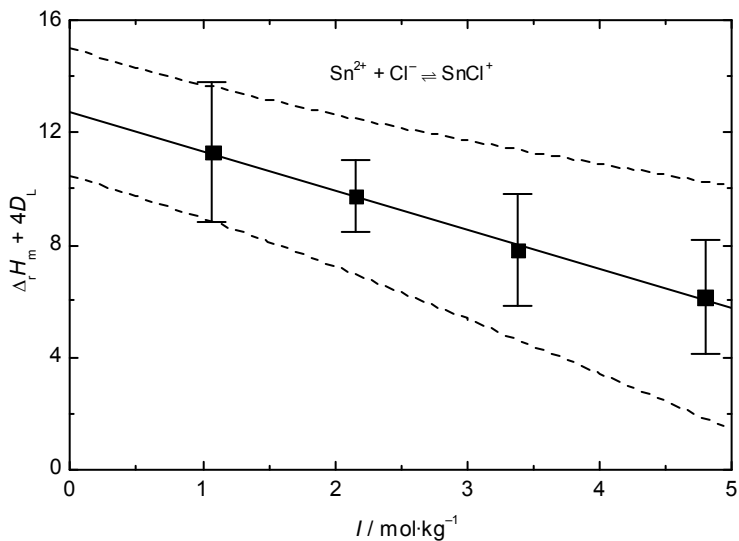
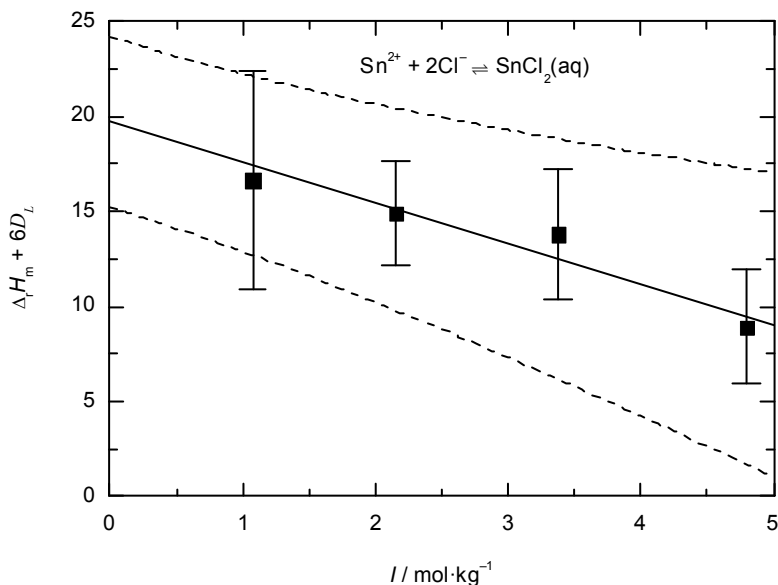


Figure VIII-23: Extrapolation to  $I = 0$  of the experimental enthalpy data for reaction  $\text{Sn}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_2(\text{aq})$  in  $\text{HClO}_4$  media. Experimental data are recalculated from [1973VAS/VAS].





From the selected reaction enthalpies, the following enthalpies of formation

$$\Delta_f H_m^\circ(\text{SnCl}^+, \text{aq}, 298.15 \text{ K}) = - (163.8 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1},$$

and

$$\Delta_f H_m^\circ(\text{SnCl}_2, \text{aq}, 298.15 \text{ K}) = - (323.9 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$$

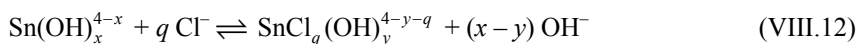
are accepted in this review.

### VIII.3.2.2 Aqueous Sn(IV) chlorides

In spite of the widely known hexachlorostannate ( $\text{SnCl}_6^{2-}$ ), very few equilibrium data are reported for the chlorido complexes of tin(IV). Moreover, the available  $\log_{10} \beta_6$  values for the reaction



( $q = 6$ ) differ from each other by more than 10 logarithmic units (*e.g.*  $\log_{10} \beta_6 = 1.6$  [1981CHE2] and 12.4 [1978FAT/ROU]). The reason of this divergence is probably the strong tendency of tin(IV) to hydrolysis. Due to the presence of hydroxido complexes, in moderately acidic solutions, only conditional equilibrium constants



can be determined, which are obviously much smaller than those of the parent chlorido complexes. A Mössbauer spectroscopic study performed by Khrarov *et al.* indicated, that the two major species (~ 30-35%) in 1 M HCl solution of tin(IV) are the complexes  $\text{SnCl}_4(\text{OH})_2^{2-}$  and  $\text{SnCl}_3(\text{OH})_3^{2-}$  [1991KHR/ZAP]. Fatouros *et al.* found that the complete suppression of the hydrolysis of tin(IV) can be achieved only in a 5 M perchloric acid solution [1978FAT/ROU], and this observation was confirmed by [2009GAJ/SIP], too.

Due to the lack of selected data for the hydrolysis of tin(IV) in acidic solutions, as well as some experimental details, the experimental data reported in [1972DES/JOV], [1981CHE2], [1989MAO/YOU2], [1991KHR/ZAP] and [1992TAY/COD] cannot be re-evaluated. Until very recently, the only reliable data set was reported by [1978FAT/ROU] based on potentiometric measurements for  $I = 5.0 \text{ M}$   $\text{HClO}_4$  background electrolyte (Table VIII-10). In connection with the determination of standard electrode potential  $E^\ominus(\text{Sn}^{4+}/\text{Sn}^{2+})$ , the formation constants of the tin(IV)-chlorido complexes were determined by spectrophotometry in [2009GAJ/SIP] at five different  $\text{HClO}_4$  concentrations (4.5 to 8.0 M), and were extrapolated to zero ionic strength (Table VIII-10).

Table VIII-10: Experimental formation constants of the species  $\text{SnCl}_q^{4-q}$ .

Method	Ionic media	$\log_{10} \beta_q$ reported	$\log_{10} \beta_q$ recalc. <sup>(a)</sup>	$\log_{10} \beta_q$ accepted <sup>(b)</sup>	Reference
$\text{Sn}^{4+} + \text{Cl}^- \rightleftharpoons \text{SnCl}^{3+}$					
Ise-Sn	$\approx 4 \text{ M (HCl, NaSO}_4, \text{H}_2\text{SO}_4)$	3.62			[1972DES/JOV]
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	3.71	$3.70 \pm 0.06$	$3.59 \pm 0.30$	[1978FAT/ROU]
sp	5.62 m HClO <sub>4</sub>	$2.91 \pm 0.36$		$2.91 \pm 0.36$	[2009GAJ/SIP]
	7.42 m HClO <sub>4</sub>	$2.80 \pm 0.30$		$2.80 \pm 0.30$	
	8.12 m HClO <sub>4</sub>	$3.13 \pm 0.12$		$3.13 \pm 0.12$	
	10.03 m HClO <sub>4</sub>	$3.52 \pm 0.15$		$3.52 \pm 0.15$	
	12.18 m HClO <sub>4</sub>	$4.40 \pm 0.30$		$4.40 \pm 0.30$	
	$\rightarrow 0^{(c)}$	$3.19 \pm 0.50$		$3.19 \pm 0.50$	
	$\rightarrow 6.41 \text{ m HClO}_4^{(d)} \leftarrow$	$2.73 \pm 0.17$		$2.73 \pm 0.17$	
$\text{Sn}^{4+} + 2 \text{Cl}^- \rightleftharpoons \text{SnCl}_2^{2+}$					
Ise-Sn	$\approx 4 \text{ M (HCl, NaSO}_4, \text{H}_2\text{SO}_4)$	4.76			[1972DES/JOV]
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	6.46	$6.46 \pm 0.04$	$6.24 \pm 0.30$	[1978FAT/ROU]
sp	5.62 m HClO <sub>4</sub>	$4.96 \pm 0.36$		$4.96 \pm 0.36$	[2009GAJ/SIP]
	7.42 m HClO <sub>4</sub>	$5.19 \pm 0.30$		$5.19 \pm 0.30$	
	8.12 m HClO <sub>4</sub>	$5.77 \pm 0.10$		$5.77 \pm 0.10$	
	10.03 m HClO <sub>4</sub>	$6.57 \pm 0.12$		$6.57 \pm 0.12$	
	12.18 m HClO <sub>4</sub>	$7.45 \pm 0.15$		$7.45 \pm 0.15$	
	$\rightarrow 0^{(c)}$	$5.95 \pm 0.36$		$5.95 \pm 0.36$	
	$\rightarrow 6.41 \text{ m HClO}_4^{(d)} \leftarrow$	$5.08 \pm 0.14$		$5.08 \pm 0.14$	
$\text{Sn}^{4+} + 3 \text{Cl}^- \rightleftharpoons \text{SnCl}_3^+$					
Ise-Sn	$\approx 4 \text{ M (HCl, NaSO}_4, \text{H}_2\text{SO}_4)$	4.71			[1972DES/JOV]
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	8.78	$8.76 \pm 0.07$	$8.44 \pm 0.30$	[1978FAT/ROU]
$\text{Sn}^{2+} + 4 \text{Cl}^- \rightleftharpoons \text{SnCl}_4(\text{aq})$					
Ise-Sn	$\approx 4 \text{ M (HCl, NaSO}_4, \text{H}_2\text{SO}_4)$	4.33			[1972DES/JOV]
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	9.48	$9.57 \pm 0.30$	$9.14 \pm 0.30$	[1978FAT/ROU]
sp	5.62 m HClO <sub>4</sub>	$8.01 \pm 0.30$		$8.01 \pm 0.30$	[2009GAJ/SIP]
	7.42 m HClO <sub>4</sub>	$8.75 \pm 0.30$		$8.75 \pm 0.30$	
	8.12 m HClO <sub>4</sub>	$9.27 \pm 0.12$		$9.27 \pm 0.12$	
	10.03 m HClO <sub>4</sub>	$10.39 \pm 0.10$		$10.39 \pm 0.10$	
	12.18 m HClO <sub>4</sub>	$11.69 \pm 0.10$		$11.69 \pm 0.10$	
	$\rightarrow 0^{(c)}$	$9.57 \pm 0.32$		$9.57 \pm 0.32$	
	$\rightarrow 6.41 \text{ m HClO}_4^{(d)} \leftarrow$	$8.31 \pm 0.14$		$8.31 \pm 0.14$	

(Continued on next page)

Table VIII-10 (continued)

Method	Ionic media	$\log_{10} \beta_q$ reported	$\log_{10} \beta_q$ recalc. <sup>(a)</sup>	$\log_{10} \beta_q$ accepted <sup>(b)</sup>	Reference
$\text{Sn}^{2+} + 5 \text{Cl}^- \rightleftharpoons \text{SnCl}_5^-$					
Ise-Sn	$\approx 4 \text{ M (HCl, NaSO}_4, \text{H}_2\text{SO}_4)$	4.40			[1972DES/JOV]
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	11.23	11.16 ± 0.20	10.62 ± 0.30	[1978FAT/ROU]
sp	5.62 m HClO <sub>4</sub>	8.91 ± 0.45		8.91 ± 0.45	[2009GAJ/SIP]
	7.42 m HClO <sub>4</sub>	9.81 ± 0.40		9.81 ± 0.40	
	8.12 m HClO <sub>4</sub>	10.20 ± 0.15		10.20 ± 0.15	
	10.03 m HClO <sub>4</sub>	11.38 ± 0.10		11.38 ± 0.10	
	12.18 m HClO <sub>4</sub>	12.43 ± 0.12		12.43 ± 0.12	
	→ 0 <sup>(c)</sup>	10.93 ± 0.41		10.93 ± 0.41	
	→ 6.41 m HClO <sub>4</sub> <sup>(d)</sup> ←	9.38 ± 0.17		9.38 ± 0.17	
$\text{Sn}^{2+} + 6 \text{Cl}^- \rightleftharpoons \text{SnCl}_6^{2-}$					
Ise-Cl	5 M (6.41 m) HClO <sub>4</sub>	12.4	12.42 ± 0.07	11.75 ± 0.30	[1978FAT/ROU]
Mössb <sup>(e)</sup>	→ 0 (HCl)	1.6			[1981CHE2]
sp	5.62 m HClO <sub>4</sub>	8.40 ± 0.50		8.40 ± 0.50	[2009GAJ/SIP]
	7.42 m HClO <sub>4</sub>	9.89 ± 0.40		9.89 ± 0.40	
	8.12 m HClO <sub>4</sub>	10.15 ± 0.18		10.15 ± 0.18	
	10.03 m HClO <sub>4</sub>	11.69 ± 0.12		11.69 ± 0.12	
	12.18 m HClO <sub>4</sub>	12.67 ± 0.15		12.67 ± 0.15	
	→ 0 <sup>(c)</sup>	9.83 ± 0.49		9.83 ± 0.49	
	→ 6.41 m HClO <sub>4</sub> <sup>(d)</sup> ←	9.28 ± 0.20		9.28 ± 0.20	

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

(c) Extrapolation to zero ionic strength by weighted linear regression and error propagation assuming Gaussian probability distribution, and 95% confidence limits of parameters.

(d) Interpolation to average ionic strength  $I_m = 6.41 \text{ mol} \cdot \text{kg}^{-1}$ .

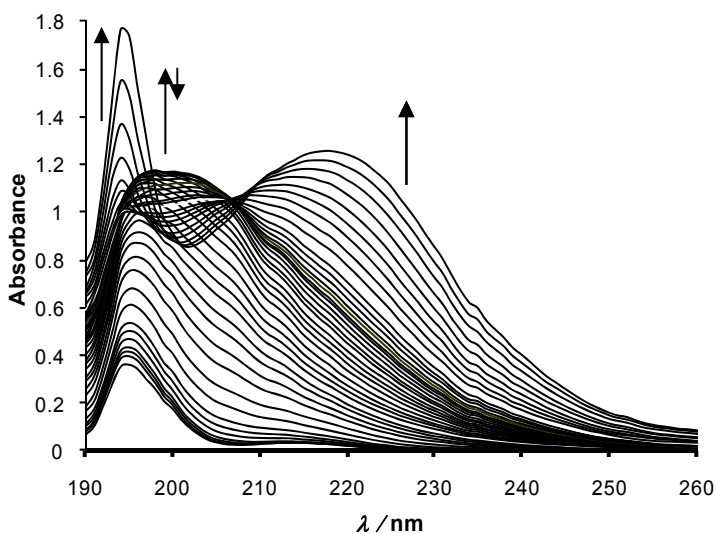
(e) Mössbauer spectroscopy.

The constants reported by [1978FAT/ROU] and [2009GAJ/SIP] confirm the expected high stability of tin(IV)-chlorido complexes, although the numerical values are rather different. Fatouros *et al.* reported non-regular tendency of stepwise stability constants ( $\log_{10} K_3 = 2.32$ ,  $\log_{10} K_4 = 0.7$ ,  $\log_{10} K_5 = 1.75$  [1978FAT/ROU]). The surprising consequence of these data is that SnCl<sub>4</sub>(aq) is only a minor species (max. 10%) in the proposed speciation scheme. Moreover,  $\log_{10} K_4 \ll \log_{10} K_5$  would indicate change in the coordination geometry during the reaction  $\text{SnCl}_3^+ + \text{Cl}^- \rightleftharpoons \text{SnCl}_4(\text{aq})$ . However, <sup>119</sup>Sn NMR chemical shifts indicate octahedral geometry for all tin(IV)-

chlorido complexes [1992TAY/COD], thus monotone decrease of the stepwise formation constants can be expected. Since the data published in [2009GAJ/SIP] are more complete (the  $\log_{10} \beta_q$  values are reported for five different ionic strengths) the selection in this review is based on the latter publication.

Figure VIII-24 shows the background and dilution corrected UV spectra of tin(IV) detected at different chloride concentration in 8 M HClO<sub>4</sub> solution. With increasing  $[\text{Cl}^-]_{\text{TOT}}$  significant spectral changes were observed, reflecting changes in the coordination sphere of tin(IV), which provided sufficient information to derive the formation constants of the tin(IV)-chlorido complexes. The observed spectral changes were best described by the formation of 5 species ( $\text{SnCl}_3^+$ ,  $\text{SnCl}_2^{2+}$ ,  $\text{SnCl}_4(\text{aq})$ ,  $\text{SnCl}_5^-$  and  $\text{SnCl}_6^{2-}$ ) at all ionic strengths.

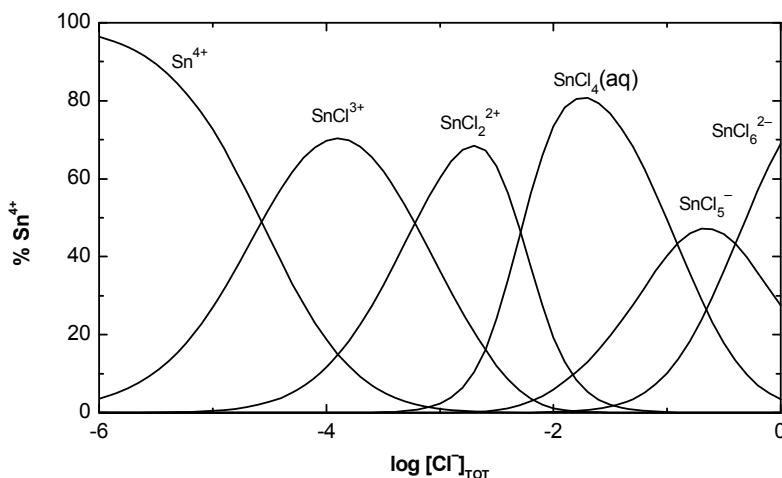
Figure VIII-24: UV-Spectral changes of tin(IV)-perchlorate solution upon addition of chloride ion ( $I_c = 8 \text{ M H}(\text{ClO}_4, \text{Cl})$ ,  $[\text{Sn}(\text{IV})]_{\text{TOT}} = 0.221 \text{ mM}$ ,  $[\text{Cl}^-]_{\text{TOT}} = 0 \text{ to } 0.32 \text{ M}$ ).



The formation of  $\text{SnCl}_3^+$  was not detected. Since  $^{119}\text{Sn}$  NMR spectra of concentrated  $\text{SnCl}_4$  solution seem to prove the existence of this species [1992TAY/COD], the former observation is probably due to the high similarity of the individual spectrum of  $\text{SnCl}_3^+$  and  $\text{SnCl}_4(\text{aq})$ , which prevents their differentiation by the method used.

The species distribution curves calculated for 8 M HClO<sub>4</sub> background electrolyte are depicted in Figure VIII-25.

Figure VIII-25: Species distribution curves of Sn(IV) chlorido complexes.



The formation constants listed in Table VIII-10 have been used to extrapolate to  $I = 0$  by weighted linear regression and error propagation assuming Gaussian probability distribution applying the Specific Ion interaction Theory (see Appendix A). The resulting thermodynamic constants are also listed in Table VIII-10. Obviously, the extrapolation to  $I = 0$  using data for  $I_m \geq 5.55 \text{ mol} \cdot \text{kg}^{-1}$  results in higher uncertainties than predicted for the range of ionic strengths were the actual measurements were carried out. Therefore, the authors preferred to define an additional key ionic strength within the range covered. The interpolated formation constants at  $I_m = 6.41 \text{ mol} \cdot \text{kg}^{-1}$  (5 M HClO<sub>4</sub>) using weighted linear regression are also listed in Table VIII-10. The following thermodynamic formation constants have been determined

$$\log_{10} \beta_1^0 \text{ ((VIII.11), } q = 1, 298.15 \text{ K)} = (3.19 \pm 0.50).$$

$$\log_{10} \beta_2^0 \text{ ((VIII.11), } q = 2, 298.15 \text{ K)} = (5.95 \pm 0.36).$$

$$\log_{10} \beta_4^0 \text{ ((VIII.11), } q = 4, 298.15 \text{ K)} = (9.57 \pm 0.32)$$

$$\log_{10} \beta_5^0 \text{ ((VIII.11), } q = 5, 298.15 \text{ K)} = (10.93 \pm 0.41).$$

$$\log_{10} \beta_6^0 \text{ ((VIII.11), } q = 6, 298.15 \text{ K)} = (9.83 \pm 0.49).$$

(for the corresponding  $\Delta \varepsilon$  values see Appendix A).

The above listed selected thermodynamic formation constants correspond to

$$\Delta_r G_m^0 \text{ ((VIII.11), } q = 1, 298.15 \text{ K)} = -(18.2 \pm 2.9) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^0 \text{ ((VIII.11), } q = 2, 298.15 \text{ K)} = -(33.9 \pm 2.1) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^\circ((\text{VIII.11}), q = 4, 298.15 \text{ K}) = -(54.6 \pm 1.8) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^\circ((\text{VIII.11}), q = 5, 298.15 \text{ K}) = -(62.3 \pm 2.3) \text{ kJ mol}^{-1},$$

$$\Delta_r G_m^\circ((\text{VIII.11}), q = 6, 298.15 \text{ K}) = -(56.1 \pm 2.8) \text{ kJ mol}^{-1}.$$

### VIII.3.3 Aqueous bromide complexes

#### VIII.3.3.1 Aqueous Sn(II) bromides

Experimental equilibrium data on the bromide complexes of tin(II) obtained from potentiometric [1928PRY], [1952VAN], [1969FED/BOL], [1975FED/BOL], [1976SAM/LYA], kinetic [1951DUK/PIN] and voltammetric [1981PET/MIL] investigations are reported for the following reactions



The formation of six bromido complexes ( $q = 1$  to  $6$ ) was reported in [1969FED/BOL]. However, the re-evaluation of the experimental data reported in [1969FED/BOL] indicated, that up to  $I = 4 \text{ M}$  the potentiometric data can be well reproduced considering the formation of the species  $\text{SnBr}^+$ ,  $\text{SnBr}_2(\text{aq})$  and  $\text{SnBr}_3^-$ . At higher ionic strength ( $I > 4 \text{ M}$ ) higher excess of bromide over tin(II) can be achieved, therefore a further complex ( $\text{SnBr}_4^{2-}$ ) should be also taken into account. The experimental data of Prytz [1928PRY] and Vanderzee [1952VAN] were also re-analyzed, while the constants reported in [1976SAM/LYA] and [1981PET/MIL] were not considered in this review (see Appendix A). The formation constants determined for  $25 \text{ }^\circ\text{C}$  and  $I \leq 6 \text{ M}$  were extrapolated to zero ionic strength using the SIT. The weighted linear regression of the eight available data for  $\text{SnBr}^+$  (Figure VIII-26), resulted in the following selected values

$$\log_{10} \beta_1^\circ((\text{VIII.13}), q = 1, 298.15 \text{ K}) = (1.33 \pm 0.18)$$

and  $\Delta \alpha((\text{VIII.13}), q = 1) = -(0.10 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ . From the latter value, the ion interaction coefficient  $\alpha(\text{SnBr}^+, \text{ClO}_4^-) = (0.15 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$  is calculated.

The SIT treatment (Figure VIII-27 and Figure VIII-28) of the accepted formation constants for the Reactions ((VIII.13),  $q = 2$  and  $3$ ) resulted in the selected values:

$$\log_{10} \beta_2^\circ((\text{VIII.13}), q = 2, 298.15 \text{ K}) = (1.97 \pm 0.21)$$

and

$$\log_{10} \beta_3^\circ((\text{VIII.13}), q = 3, 298.15 \text{ K}) = (1.93 \pm 0.27).$$

Figure VIII-26: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{Br}^- \rightleftharpoons \text{SnBr}^+$  in  $\text{NaClO}_4$  media. Experimental data from [1928PRY], [1951DUK/PIN], [1952VAN], [1969FED/BOL] and [1975FED/BOL].

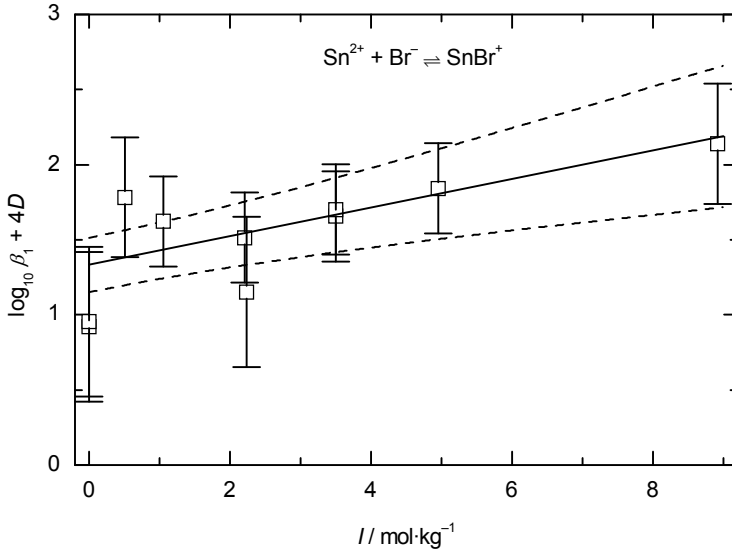


Figure VIII-27: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 2 \text{Br}^- \rightleftharpoons \text{SnBr}_2(\text{aq})$  in  $\text{NaClO}_4$  media. Experimental data from [1928PRY], [1952VAN], [1969FED/BOL] and [1975FED/BOL].

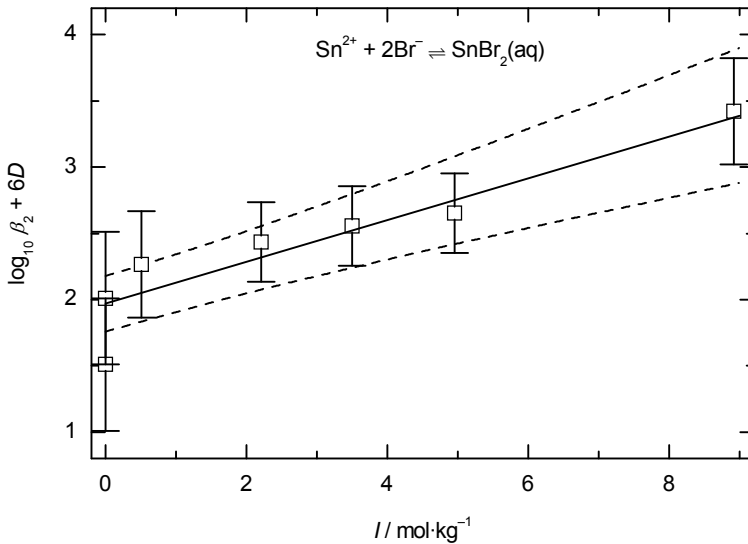
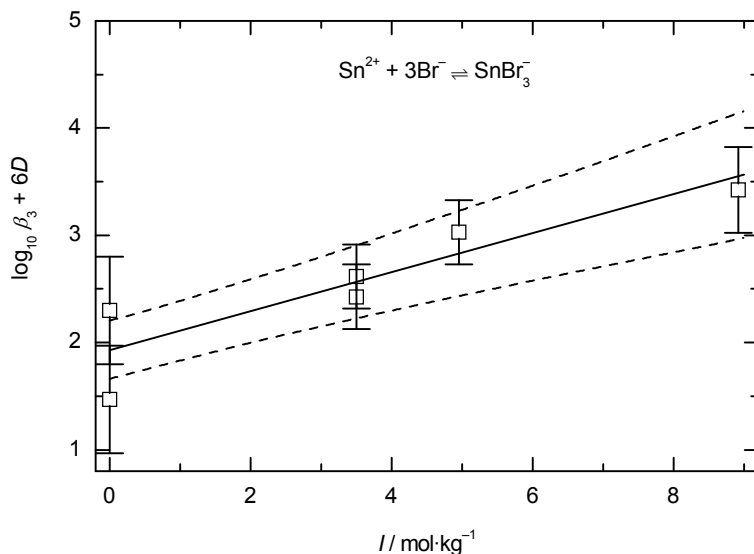


Figure VIII-28: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 3 \text{Br}^- \rightleftharpoons \text{SnBr}_3^-$  in  $\text{NaClO}_4$  media. Experimental data from [1928PRY], [1952VAN], and [1969FED/BOL].



The corresponding ion interaction coefficients are  $\Delta\epsilon(\text{VIII.13}, q = 2) = -(0.16 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  and  $\Delta\epsilon(\text{VIII.13}, q = 3) = -(0.18 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ , respectively. From these values  $\epsilon(\text{SnBr}_2(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.14 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$  and  $\epsilon(\text{Na}^+, \text{SnBr}_3^-) = (0.16 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$  can be derived. As described in Appendix B, interaction coefficients for neutral species like  $\epsilon(\text{SnBr}_2(\text{aq}), \text{NaClO}_4(\text{aq}))$  are expected to be generally small, but when data make possible to determine them as in the current case, the value has to be reported.

The selected thermodynamic formation constants correspond to

$$\Delta_f G_m^\circ (\text{VIII.13}, q = 1, 298.15 \text{ K}) = -(7.6 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{VIII.13}, q = 2, 298.15 \text{ K}) = -(11.2 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{VIII.13}, q = 3, 298.15 \text{ K}) = -(11.0 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1},$$

and hence

$$\Delta_f G_m^\circ (\text{SnBr}^+, \text{aq}, 298.15 \text{ K}) = -(138.8 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{SnBr}_2, \text{aq}, 298.15 \text{ K}) = -(246.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{SnBr}_3^-, \text{aq}, 298.15 \text{ K}) = -(350.0 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}.$$



Vanderzee studied the complex formation processes at  $I = 3 \text{ M}$  and at four different temperatures [1952VAN]. The recalculated formation constants (Table VIII-11) were used to derive reaction enthalpies of the Reactions ((VIII.13),  $q = 1, 2, 3$ ):  $\Delta_r H_m^\circ$  (VIII.13) =  $(5.1 \pm 2.0)$ ,  $(12.9 \pm 2.0)$  and  $(7.2 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively (see Appendix A). The heats of the Reactions ((VIII.13),  $q = 1, 2$ ) show distinct ionic strength dependence (Figure VIII-27 and Figure VIII-28). Since similar behaviour can be expected in case of bromide for the Reactions ((VIII.13),  $q = 1, 2, 3$ ), the above reactions enthalpies cannot be recommended as selected standard values, but can be used as estimates.

Table VIII-11: Experimental formation constants of the species  $\text{SnBr}_q^{2-q}$ .

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{Br}^- \rightleftharpoons \text{SnBr}^+$						
Ise-Sn	0 corr ((H/K)Br)	25	1.11	0.92	$0.92 \pm 0.50$	[1928PRY]
kin	2.03 M HClO <sub>4</sub>	25	0.43		$0.37 \pm 0.50$ <sup>(c)</sup>	[1951DUK/PIN]
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	0.63	$0.64 \pm 0.02$	$0.57 \pm 0.30$	[1952VAN]
		25	0.73	$0.73 \pm 0.01$	$0.66 \pm 0.30$	
		35	0.76	$0.75 \pm 0.01$	$0.68 \pm 0.30$	
		45	0.79	$0.78 \pm 0.03$	$0.71 \pm 0.30$	
Ise-Sn	1.0 M NaClO <sub>4</sub> 2.0 M NaClO <sub>4</sub> 3.0 M NaClO <sub>4</sub> 4.0 M NaClO <sub>4</sub> 6.0 M NaClO <sub>4</sub> 8.0 M NaClO <sub>4</sub>	25	$0.74 \pm 0.04$	$0.82 \pm 0.01$	$0.80 \pm 0.30$	[1969FED/BOL]
		25	$0.57 \pm 0.07$	$0.62 \pm 0.01$	$0.58 \pm 0.30$	
		25	$0.78 \pm 0.02$	$0.77 \pm 0.01$	$0.70 \pm 0.30$	
		25	$0.85 \pm 0.02$	$0.89 \pm 0.02$	$0.80 \pm 0.30$	
		25	$1.18 \pm 0.03$	$1.20 \pm 0.02$	$1.03 \pm 0.40$	
		25	$1.60 \pm 0.04$	$1.45 \pm 0.14$		
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	$1.09 \pm 0.10$		$1.08 \pm 0.40$	[1975FED/BOL]
Ise-Sn	1.0 M LiClO <sub>4</sub>	25	$0.95 \pm 0.06$			[1976SAM/LYA]
vlt	1.0 M NaNO <sub>3</sub> 0 corr (NaBr)	25	$0.60 \pm 0.10$	$0.61 \pm 0.13$		[1981PET/MIL]
		25		$0.95 \pm 0.50$	$0.95 \pm 0.50$	
Möss <sup>(d)</sup>	3.5 M (Na,H)(ClO <sub>4</sub> ,Br)	<sup>(e)</sup>	1.34			[1984HSU/CHE]
$\text{Sn}^{2+} + 2 \text{Br}^- \rightleftharpoons \text{SnBr}_2(\text{aq})$						
Ise-Sn	0 corr ((H/K)Cl)	25	1.81	1.51	$1.51 \pm 0.50$	[1928PRY]
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	0.95	$0.90 \pm 0.11$	$0.77 \pm 0.30$	[1952VAN]
		25	1.14	$1.10 \pm 0.04$	$0.97 \pm 0.30$	
		35	1.19	$1.18 \pm 0.01$	$1.05 \pm 0.30$	
		45	1.27	$1.25 \pm 0.09$	$1.12 \pm 0.30$	

(Continued on next page)

Table VIII-11 (continued)

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	0.90 ± 0.07			[1969FED/BOL]
	2.0 M NaClO <sub>4</sub>	25	1.19 ± 0.01	1.12 ± 0.01	1.03 ± 0.30	
	3.0 M NaClO <sub>4</sub>	25	1.17 ± 0.02	1.19 ± 0.02	1.06 ± 0.30	
	4.0 M NaClO <sub>4</sub>	25	1.43 ± 0.07	1.27 ± 0.06	1.08 ± 0.30	
	6.0 M NaClO <sub>4</sub>	25	2.11 ± 0.11	2.10 ± 0.04	1.76 ± 0.40	
	8.0 M NaClO <sub>4</sub>	25	2.74 ± 0.04	2.89 ± 0.09		
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	1.23 ± 0.12		1.21 ± 0.40	[1975FED/BOL]
Ise-Sn	1.0 M LiClO <sub>4</sub>	25	1.24 ± 0.04			[1976SAM/LYA]
vlt	1.0 M NaNO <sub>3</sub>	25	1.13 ± 0.10	1.09 ± 0.09		[1981PET/MIL]
	0 corr (NaBr)	25		2.01 ± 0.50	2.01 ± 0.50	
Möss ( <sup>d</sup> )	3.5 M (Na <sub>3</sub> H)(ClO <sub>4</sub> ,Br)	<sup>(e)</sup>	1.82			[1984HSU/CHE]
$\text{Sn}^{2+} + 3 \text{Br}^- \rightleftharpoons \text{SnBr}_3^-$						
Ise-Sn	0 corr ((H/K)Cl)	25	1.46	1.47	1.47 ± 0.50	[1928PRY]
Ise-Sn	3 M (H/Na)ClO <sub>4</sub>	0	1.36	1.39 ± 0.08	1.19 ± 0.30	[1952VAN/RHO]
		25	1.68	1.59 ± 0.16	1.39 ± 0.30	
		35	1.83	1.67 ± 0.24	1.47 ± 0.30	
		45	1.95	1.90 ± 0.14	1.70 ± 0.30	
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	1.09 ± 0.03	1.13 ± 0.04	0.93 ± 0.30	[1969FED/BOL]
		25	1.48 ± 0.05	1.74 ± 0.04	1.46 ± 0.30	
		25	2.18 ± 0.10	2.58 ± 0.04	1.98 ± 0.30	
		25	3.74 ± 0.05	3.72 ± 0.05		
Ise-Sn	1.0 M LiClO <sub>4</sub>	25	1.38 ± 0.07			[1976SAM/LYA]
vlt	0 corr (NaBr)	25		2.30 ± 0.50	2.30 ± 0.50	[1981PET/MIL]
Möss ( <sup>d</sup> )	3.5 M (Na <sub>3</sub> H)(ClO <sub>4</sub> ,Br)	<sup>(e)</sup>	1.42			[1984HSU/CHE]
$\text{Sn}^{2+} + 4 \text{Br}^- \rightleftharpoons \text{SnBr}_4^{2-}$						
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	0.40 ± 0.06			[1969FED/BOL]
		25	1.00 ± 0.05			
		25	2.18 ± 0.18	2.20 ± 0.08		
		25	3.30 ± 0.05	3.48 ± 0.06		
$\text{Sn}^{2+} + 5 \text{Br}^- \rightleftharpoons \text{SnBr}_5^{3-}$						
Ise-Sn	8.0 M NaClO <sub>4</sub>	25	2.40 ± 0.15			[1969FED/BOL]

(Continued on next page)

Table VIII-11 (continued)

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + 6 \text{Br}^- \rightleftharpoons \text{SnBr}_6^{4-}$						
Ise-Sn	8.0 M NaClO <sub>4</sub>	25	2.28 ± 0.13			[1969FED/BOL]

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

(c) Corrected to NaClO<sub>4</sub> medium.

(d) Mössbauer spectroscopy.

(e) Equilibrated at room temperature, then measured in a fast-frozen solution.

### VIII.3.3.2 Aqueous Sn(IV) bromides

The complex formation processes in the aqueous tin(IV)-bromide system have been investigated by <sup>119</sup>Sn NMR spectroscopy [1992TAY/COD]. Since the speciation suggested by the authors does not involve partially hydrolysed bromido complexes (see also Section VIII.3), reliable thermodynamic data cannot be extracted from [1992TAY/COD].

## VIII.3.4 Aqueous iodide complexes

### VIII.3.4.1 Aqueous Sn(II) iodides

Formation constants of Sn(II) iodide complexes according to the reaction



have been reported only in [1976SAM/LYA] and [1968HAI/JOH]. The constants reported in [1976SAM/LYA] were not considered in this review (see Appendix A). Based on their solubility measurements made in 4 M NaClO<sub>4</sub> solution, Haight and Johansson [1968HAI/JOH] suggested the formation of six iodido complexes with  $q = 1, 2, 3, 4, 6$  and  $8$ . The re-evaluation of the experimental data indicated that four species ( $\text{SnI}_q^{2-q}$ ,  $q = 1, 2, 3, 4$ ) are sufficient to describe the experimental data up to  $[\text{I}^-]_{\text{tot}} = 0.6 \text{ M}$  (15% replacement of the background electrolyte). The reported and recalculated constants are listed in Table VIII-12. It should be noted, that the consideration of at least one additional complex (*e.g.*  $\text{SnI}_5^{3-}$ ) is necessary to fit the solubility data at  $[\text{I}^-]_{\text{tot}} > 0.6 \text{ M}$ . However, the correct re-evaluation of the experimental data for  $[\text{I}^-]_{\text{tot}} > 0.6 \text{ M}$  is hindered by the probably important medium effect, caused by the replacement of the background electrolyte (NaClO<sub>4</sub>) by NaI. Therefore further studies are required to establish the composition and stability of the formed complexes at higher iodide

concentrations. Since reliable experimental data are available only for  $I = 4.0$  M, thermodynamic formation constants cannot be selected.

Table VIII-12: Experimental formation constants of the species  $\text{SnI}_q^{2-q}$ .

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{I}^- \rightleftharpoons \text{SnI}^+$						
sol	4.0 M NaClO <sub>4</sub>	25	$0.7 \pm 0.05$	$0.75 \pm 0.30$	$0.75 \pm 0.30$	[1968HAI/JOH]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	$0.76 \pm 0.02$			[1976SAM/LYA]
$\text{Sn}^{2+} + 2 \text{I}^- \rightleftharpoons \text{SnI}_2(\text{aq})$						
sol	4.0 M NaClO <sub>4</sub>	25	$1.13 \pm 0.07$	$1.14 \pm 0.30$	$1.14 \pm 0.30$	[1968HAI/JOH]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	$1.15 \pm 0.07$			[1976SAM/LYA]
$\text{Sn}^{2+} + 3 \text{I}^- \rightleftharpoons \text{SnI}_3^-$						
sol	4.0 M NaClO <sub>4</sub>	25	$2.13 \pm 0.03$	$1.60 \pm 0.30$	$1.60 \pm 0.30$	[1968HAI/JOH]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	$2.10 \pm 0.04$			[1976SAM/LYA]
$\text{Sn}^{2+} + 4 \text{I}^- \rightleftharpoons \text{SnI}_4^{2-}$						
sol	4.0 M NaClO <sub>4</sub>	25	$2.30 \pm 0.04$	$2.69 \pm 0.50$	$2.69 \pm 0.50$	[1968HAI/JOH]
$\text{Sn}^{2+} + 6 \text{I}^- \rightleftharpoons \text{SnI}_6^{4-}$						
sol	4.0 M NaClO <sub>4</sub>	25	$2.59 \pm 0.02$			[1968HAI/JOH]
$\text{Sn}^{2+} + 8 \text{I}^- \rightleftharpoons \text{SnI}_8^{6-}$						
sol	4.0 M NaClO <sub>4</sub>	25	$2.08 \pm 0.04$			[1968HAI/JOH]

(a) Re-evaluated values (see Appendix A), the uncertainties are estimated by the reviewers.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

### VIII.3.4.2 Aqueous tin(IV) iodides

Apparently, no thermodynamic data are available for the aqueous iodido complexes of tin(IV).

## VIII.3.5 Mixed halogen complexes

### VIII.3.5.1 Mixed halogeno complexes of tin(II)

As mentioned in Section VIII.3, all the ten trihalogenostannate(II) anions ( $[\text{SnCl}_x\text{Br}_y\text{I}_z]^-$ ,  $x + y + z = 3$ ) have been identified by <sup>119</sup>Sn NMR in [1989COD/TAY]. However, thermodynamic data are available only for the chlorido-bromido ternary complexes (Table VIII-13). The broader sense of mixed halogeno complexes includes the

thiocyanato complexes, too, therefore the equilibrium data for the chlorido-thiocyanato complexes are also enumerated in Table VIII-13. Both in [1975FED/BOL] and [1980FED/BOL], the NaClO<sub>4</sub> medium was entirely replaced during the measurements of the ternary complexes, inducing considerable changes in the activities. The re-evaluation of the potentiometric data reported in [1975FED/BOL] and [1980FED/BOL] was unsuccessful, probably due to the low precision of the graphically presented experimental data. Therefore, the data listed in Table VIII-13, although informative, cannot be used to derive selected values.

Table VIII-13: Experimental formation constants of the mixed halogeno complexes of tin(II).

Method	Ionic media	<i>t</i> /°C	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{Cl}^- + \text{Br}^- \rightleftharpoons \text{SnClBr}(\text{aq})$						
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	2.13 ± 0.13		[1975FED/BOL]	
	1.0 M NaClO <sub>4</sub>	25	1.64 ± 0.09			
	3.0 M NaClO <sub>4</sub>	25	1.93 ± 0.03			
	4.0 M NaClO <sub>4</sub>	25	2.13 ± 0.04			
	6.0 M NaClO <sub>4</sub>	25	2.40 ± 0.05			
$\text{Sn}^{2+} + 2 \text{Cl}^- + \text{Br}^- \rightleftharpoons \text{SnCl}_2\text{Br}^-$						
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	1.98 ± 0.03		[1975FED/BOL]	
	4.0 M NaClO <sub>4</sub>	25	2.44 ± 0.10			
	6.0 M NaClO <sub>4</sub>	25	3.73 ± 0.06			
$\text{Sn}^{2+} + \text{Cl}^- + 2 \text{Br}^- \rightleftharpoons \text{SnClBr}_2^-$						
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	1.37 ± 0.15		[1975FED/BOL]	
	4.0 M NaClO <sub>4</sub>	25	2.19 ± 0.10			
	6.0 M NaClO <sub>4</sub>	25	3.43 ± 0.09			
$\text{Sn}^{2+} + \text{Cl}^- + \text{SCN}^- \rightleftharpoons \text{SnCl}(\text{SCN})(\text{aq})$						
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	1.90 ± 0.10		[1980FED/BOL]	
	1.0 M NaClO <sub>4</sub>	25	1.51 ± 0.06			
	3.0 M NaClO <sub>4</sub>	25	1.87 ± 0.10			
$\text{Sn}^{2+} + 2 \text{Cl}^- + \text{SCN}^- \rightleftharpoons \text{SnCl}_2(\text{SCN})^-$						
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	2.18 ± 0.06		[1980FED/BOL]	
$\text{Sn}^{2+} + \text{Cl}^- + 2 \text{SCN}^- \rightleftharpoons \text{SnClSCN}_2^-$						
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	0.78 ± 0.10		[1980FED/BOL]	
	3.0 M NaClO <sub>4</sub>	25	1.91 ± 0.10			

(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

### VIII.3.5.2 Mixed halogeno complexes of tin(IV)

Mixed halogeno complexes form readily in case of tin(IV), too. In the aqueous solution of  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ ,  $\text{LiCl}$  and  $\text{LiBr}$  at least 20  $^{119}\text{Sn}$  NMR resonances were detected, which were attributed to the series  $\text{SnCl}_x\text{Br}_y(\text{H}_2\text{O})_z$  ( $x + y + z = 6$ ) complexes [1992TAY/COD]. The real situation is probably more complicated, since the aquo and hydroxo complexes are indistinguishable by NMR spectroscopy, due to the fast proton exchange. Equilibrium data for the mixed halogeno complexes have been reported only in [1968DEA/EVA], based on  $^{19}\text{F}$  NMR measurements. Their data are collected in Table VIII-14. Since these equilibrium constants were determined at high ionic strength, selected values cannot be derived. Nevertheless, the data listed in Table VIII-14 indicate decreasing binding ability of halides in the order  $\text{F}^- \gg \text{Cl}^- > \text{Br}^-$ , in agreement with the 'hard' nature of tin(IV).

Table VIII-14: Experimental formation constants of the mixed halogeno complexes of tin(IV).

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$		Reference
			Reported	Recalculated <sup>(a)</sup> Accepted <sup>(b)</sup>	
<hr/>					
$\text{SnF}_6^{2-} + \text{Cl}^- \rightleftharpoons \text{SnClF}_5^{2-} + \text{F}^-$					
NMR	1.2 M $(\text{NH}_4)_2\text{SnF}_6$ + 3 M $(\text{H}_2\text{NH}_4)\text{Cl}$	22	$-3.26 \pm 0.14$		[1968DEA/EVA]
<hr/>					
$\text{SnClF}_5^{2-} + \text{Cl}^- \rightleftharpoons \text{SnCl}_2\text{F}_4^{2-} + \text{F}^-$					
NMR	1.2 M $(\text{NH}_4)_2\text{SnF}_6$ + 3 M $(\text{H}_2\text{NH}_4)\text{Cl}$	22	$-3.89 \pm 0.04$		[1968DEA/EVA]
<hr/>					
$\text{SnF}_6^{2-} + \text{Br}^- \rightleftharpoons \text{SnBrF}_5^{2-} + \text{F}^-$					
NMR	1.2 M $(\text{NH}_4)_2\text{SnF}_6$ + 3 M $(\text{H}_2\text{NH}_4)\text{Br}$	22	$-4.24 \pm 0.20$		[1968DEA/EVA]

(a) Re-evaluated value, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

## VIII.4 Gaseous halides

### VIII.4.1 Gaseous fluorides

#### VIII.4.1.1 $\text{SnF}_2(\text{g})$

Ideal gas properties of gaseous  $\text{SnF}_2$  were calculated by [1991GUR/VEY], [1963BRE/SOM] and [1973HAU/HAS] from spectroscopic and structural data. The

data were those of [1973HAU/HAS] and [1968HAU/HAS]. The data were re-evaluated by [1991GUR/VEY], who performed the calculations using the rigid rotator-harmonic oscillator approximation.

The standard enthalpy of formation of gaseous  $\text{SnF}_2$  may be derived from data for the condensed phase compound. In Section VIII.1.1.1 the value  $\Delta_f H_m^\circ(\text{SnF}_2, \text{cr}, 298.15 \text{ K}) = -(700.6 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$  was selected. As a consequence, no acceptable datum for  $\Delta_f H_m^\circ(\text{SnF}_2, \text{g}, 298.15 \text{ K})$  may be derived.

Table VIII-15: Ideal gas properties of  $\text{SnF}_2$ , from compilations/evaluations (C/E) and original article (A).

Reference	$C_{p,m}^\circ(\text{SnF}_2, \text{g}, 298.15 \text{ K})/$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_m^\circ(\text{SnF}_2, \text{g}, 298.15 \text{ K})/$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{SnF}_2, \text{g}, 298.15 \text{ K})/$ $\text{kJ}\cdot\text{mol}^{-1}$
[1991GUR/VEY] <sup>(C/E)</sup>	49.679 <sup>(a)</sup>	282.123 <sup>(a)</sup>	- 510.957
[1993BAR] <sup>(C/E)</sup>	49.679	282.124	- 483.955
[1999BIN/MIL] <sup>(C/E)</sup>	49.65	282.1	- 484.0
[1973HAU/HAS] <sup>(A)</sup>	-	-	- 452

(a) Selected data.

The enthalpy of sublimation may be deduced from vapour pressure measurements. These measurements were reported by [1964FIS/PET] and [1969DUD/SEA]. The data were evaluated and treated by [1991GUR/VEY], whose analysis is adopted here.

Pertinent information and results are given in Table VIII-16.

Table VIII-16: Determination of the enthalpy of sublimation of  $\text{SnF}_2(\text{cr})$  from vapour pressure measurements.

Reference	Method	$T/\text{K}$	$\Delta_{\text{sub}} H_m^\circ(\text{SnF}_2, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
			2 <sup>nd</sup> law	3 <sup>rd</sup> law
[1964FIS/PET]	static	769 - 1100	150	$170.3 \pm 4.0$
[1969DUD/SEA]	torsion effusion	532 - 670	154	$162.6 \pm 1.0$

These results were obtained with the use of auxiliary thermodynamic data for  $\text{SnF}_2$  as evaluated by [1991GUR/VEY].

In neither [1964FIS/PET] nor [1969DUD/SEA] were the individual data tabulated; rather, only parameters of the equation type  $\log_{10} p = a/T + b$  were given. Fischer and Petzel [1964FIS/PET] stated that 24 data points were used; Dudash and Searcy [1969DUD/SEA] showed a plot with 83 points.

Zmbov *et al.* [1968ZMB/HAS] examined the gaseous species above liquid SnF<sub>2</sub> in the range 520 to 623 K by mass spectrometry. The third law results in Table VIII-16 involved a correction [1991GUR/VEY] for the formation of dimer molecules Sn<sub>2</sub>F<sub>4</sub> (g) of 20% of the total pressure.

The final weighted average value for the enthalpy of sublimation, selected here, is

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{SnF}_2, \text{cr}, 298.15 \text{ K}) = (166 \pm 2) \text{ kJ}\cdot\text{mol}^{-1}$$

from the preferred third-law values.

From the selected enthalpies of formation and sublimation of SnF<sub>2</sub>(cr) here given, the quantity

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnF}_2, \text{g}, 298.15 \text{ K}) = -(535 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$$

is adopted as selected value.

The selected heat-capacity data for gaseous SnF<sub>2</sub> [1991GUR/VEY] may be generated by the equation

$$[C_{p,m}^{\circ}]_{100\text{K}}^{600\text{K}}(\text{SnF}_2, \text{g}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 29.68 + 0.09146 T/\text{K} - 8.175 \times 10^{-5} (T/\text{K})^2.$$

Standard error of estimate is 0.3 J·K<sup>-1</sup>·mol<sup>-1</sup>.

Other selected data are:

$$C_{p,m}^{\circ}(\text{SnF}_2, \text{g}, 298.15 \text{ K}) = (49.7 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{SnF}_2, \text{g}, 298.15 \text{ K}) = (282.1 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

which yields:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{SnF}_2, \text{g}, 298.15 \text{ K}) = -(543.4 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### VIII.4.1.2 SnF<sub>4</sub>(g)

Thermodynamic properties given by [1991GUR/VEY] are semi-empirical estimates and there are no experimental data as a basis for evaluation.

### VIII.4.2 Gaseous chlorides

#### VIII.4.2.1 SnCl<sub>2</sub>(g)

Ideal gas properties of SnCl<sub>2</sub> were calculated by [1991GUR/VEY], [1963BRE/SOM] and [1964NAG2] from spectroscopic and structural data. The data were those of [1938ASU/KAR], [1941LIS/SUT], [1958AKI/SPI], [1964DES/PAN], [1966NAE/PAL], [1969HAS/HAU], [1969PER], [1970AND/FRE], [1970BEA/PER], [1971HUB/OZI] and [1976TEV/NAK]. Gurvich and Veyts [1991GUR/VEY]



re-evaluated the data and performed the calculations using the rigid rotator-harmonic oscillator approximation. Reported data are presented in Table VIII-17.

The standard enthalpy of formation of gaseous  $\text{SnCl}_2$  may be derived from data for the condensed phase compound. In Section VIII.1.2.1 the value

$$\Delta_f H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = - (327.9 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

was selected. The enthalpy of sublimation may be deduced from vapour pressure measurements. The data sources are summarised in Table VIII-18. Evaluated auxiliary data for  $\text{SnCl}_2$  [1991GUR/VEY] were used to derive values for the enthalpy of sublimation in Table VIII-18.

Table VIII-17: Ideal gas properties of  $\text{SnCl}_2$ , from compilations/evaluations (C/E) and original article (A).

Reference	$C_{p,m}^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K})/$	$S_m^\circ \text{SnCl}_2, \text{g}, 298.15 \text{ K})/$	$\Delta_f H_m^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K})/$
	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
[1999BIN/MIL] <sup>(C/E)</sup>	54.65	305.9	- 197.9
[1993BAR] <sup>(C/E)</sup>	54.632	305.855	- 197.945
[1991GUR/VEY] <sup>(C/E)</sup>	54.635 <sup>(a)</sup>	305.898 <sup>(a)</sup>	- 197.648 <sup>(a,b)</sup>
[1964NAG2] <sup>(A)</sup>	56.212	312.152	-

(a) Selected data.

(b) Based on  $\Delta_f H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15) = - (327.9 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$ .

Table VIII-18: Determination of the enthalpy of sublimation of  $\text{SnCl}_2(\text{cr})$  from vapour pressure measurements, neglecting dimerisation in the gas phase.

Reference	Method	$T/\text{K}$	Number of data	$\Delta_{\text{sub}} H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
				2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1939FIS/GEW2]	Static	677-902	18	121 ± 3	131.5 ± 0.8
[1939FIS/GEW]	Static	715-907	8	123 ± 7	130.3 ± 1.6
[1987MUC/OBR]	Static	599-891	78	128 ± 9	
[1967KAR/NOV]	Static	673-883	14	124 ± 1	128.3 ± 0.9
[1962BUY/SHA]	Transpiration	373-633	17	71 ± 6	114.3 ± 3.0
[1971PER2]	Boiling point	763-928	6	130 ± 2	129.5 ± 0.7

The more accurate third law values were favoured and the selected value is

$$\Delta_{\text{sub}} H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = (130.4 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$$

Hence from these two data,

$$\Delta_f H_m^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K}) = - (197.5 \pm 4.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

Other selected data are (Table VIII-17)

$$C_{p,m}^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K}) = (54.6 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K}) = (305.9 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^\circ (\text{SnCl}_2, \text{g}, 298.15 \text{ K}) = - (206.9 \pm 4.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

From mass spectrometric measurements on the vapour above solid and liquid  $\text{SnCl}_2$  [1967KAR/NOV], evidence was found for the existence of the dimer  $\text{Sn}_2\text{Cl}_4$ . This was corroborated by later more detailed measurements of [1987OBR/MUC] and [2005HIL/ROS]. Partial pressures of monomer and dimer were determined by [2005HIL/ROS] between 673 and 773 K; their data, when extrapolated, indicate that the mole fraction of dimer in the gas phase is less than 0.01 at 298 K.

#### VIII.4.2.2 $\text{SnCl}_4(\text{g})$

Ideal gas properties of gaseous  $\text{SnCl}_4$  were calculated by [1991GUR/VEY] and [1962ANA] from spectroscopic and structural data. Gurvich and Veys [1991GUR/VEY] re-evaluated a large quantity of data, the sources of which are given in Table VIII-19. The calculations were performed with the use of the rigid rotator-harmonic oscillator approximation. Reported data appear in Table VIII-20.

Table VIII-19: Data sources for the calculation of ideal gas properties of  $\text{SnCl}_4$ .

Data type	References
Electron diffraction	[1934BRO/WAL], [1935PAU/BRO], [1931WIE], [1970FUJ/KIM], [1959LIV/RAO]
Neutron diffraction	[1979GRA/STA], [1977TRI]
Spectroscopic	[1973DER], [1968BUR/RUO], [1971CLA/RIP], [1972CLA/RIP], [1972CLA/RIP2], [1954DEL/FRA], [1967GRI/PAO], [1968KEB/MUL], [1975STO/BAR], [1972THO/ORV], [1948WEL/CRA], [1978BAB/GRI], [1984ART/BEA], [1963RUL/WEB], [1964BUT/GER], [1971CLA/WIL], [1975KON/MUL], [1969LEV], [1963MOS], [1972MUL/KON]
Quantum chemical calculation	[1981PIE/BLU]
Electron-gas diffraction	[1970FUJ/KIM]

Table VIII-20: Ideal gas properties of SnCl<sub>4</sub> from compilations/evaluations (C/E) and original article (A).

Reference	$C_{p,m}^{\circ}$ (SnCl <sub>4</sub> , g, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}$ (SnCl <sub>4</sub> , g, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta_f H_m^{\circ}$ (SnCl <sub>4</sub> , g, 298.15 K)/ kJ·mol <sup>-1</sup>
[1962ANA] <sup>(A)</sup>	98.45	364.8	-
[1991GUR/VEY] <sup>(C/E)</sup>	98.400 <sup>(a)</sup>	366.872 <sup>(a)</sup>	- 478.466 <sup>(a)</sup>
[1999BIN/MIL] <sup>(C/E)</sup>	98.38	365	- 471.5
[1993BAR] <sup>(C/E)</sup>	98.452	364.954	- 471.537

(a) Selected data.

Tin tetrachloride, SnCl<sub>4</sub>(l), melts at 239.05 K [1984BER/STE]. A value for  $\Delta_f H_m^{\circ}$  (SnCl<sub>4</sub>, g, 298.15 K) may be derived from data for the liquid compound. A summary of reported data for  $\Delta_f H_m^{\circ}$  (SnCl<sub>4</sub>, l, 298.15 K), with experimental details, is given in Table VIII-21.

The selected value is the most recent one of [1974VAS/VAS],

$$\Delta_f H_m^{\circ} (\text{SnCl}_4, \text{l}, 298.15 \text{ K}) = - (517.0 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

included in Table VIII-22, which lists available data for this quantity.

Table VIII-21: Determination of the standard enthalpy of formation of SnCl<sub>4</sub>(l).

Reference	Method	$\Delta_f H_m^{\circ}$ (SnCl <sub>4</sub> , l, 298.15 K)/ kJ·mol <sup>-1</sup>
[1878BER]	Calorimetric (291 K) SnCl <sub>2</sub> (cr) + Cl <sub>2</sub> (g)	- 538.1
[1974VAS/VAS]	Calorimetric (298 K) Enthalpy of dissolution of SnCl <sub>4</sub> (l) and Sn(cr) in HClO <sub>4</sub> (or H <sub>2</sub> O <sub>2</sub> )/HCl solution	- (517.0 ± 2.0) <sup>(a)</sup>

(a) Selected value.

Table VIII-22: Thermodynamic data for SnCl<sub>4</sub>(l) from compilations/evaluations.

Reference	$C_{p,m}^{\circ}$ (SnCl <sub>4</sub> , l, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}$ (SnCl <sub>4</sub> , l, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta_f H_m^{\circ}$ (SnCl <sub>4</sub> , l, 298.15 K)/ kJ·mol <sup>-1</sup>
[1991GUR/VEY]	157.4 <sup>(a)</sup>	265.000 <sup>(a)</sup>	- 517.000 <sup>(a)</sup>
[1993BAR]	165.2	258.739	- 511.285
[1973BAR/KNA]	150.624	258.6	- 511.004
[1977BAR/KNA]	165.268	259.0	- 528.9
[1999BIN/MIL]	165.2	258.7	- 511.3

(a) Selected data

The vapour pressure of liquid  $\text{SnCl}_4$  was measured by several authors (Table VIII-23) and the enthalpy of vapourisation was derived from these data, with the use of evaluated auxiliary data for  $\text{SnCl}_4(\text{l})$  [1991GUR/VEY]. The results in Table VIII-23 are concordant, and the selected value is

$$\Delta_{\text{vap}}H_{\text{m}}^{\circ}(\text{SnCl}_4, \text{l}, 298.15 \text{ K}) = (38.5 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Table VIII-23: Enthalpy of vapourisation of  $\text{SnCl}_4(\text{l})$  as derived from vapour pressure measurements.

Reference	Method	T/K	Number of data	$\Delta_{\text{vap}}H_{\text{m}}^{\circ}(\text{SnCl}_4, \text{l}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
				2 <sup>nd</sup> law	3 <sup>rd</sup> law
[1940HIE/REI]	Static	273-371	12	$37.4 \pm 1.0$	$38.7 \pm 1.6$
[1951KAB/NYH]	Static	290-370	19	$37.3 \pm 0.9$	$38.6 \pm 1.0$
[1983SOL/GRI]	Static	290-370	(a)	39.1	$38.8 \pm 1.2$

(a) Data in equation form only.

Hence from these two data

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnCl}_4, \text{g}, 298.15 \text{ K}) = - (478.5 \pm 3.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Other selected data are

$$C_{p,\text{m}}^{\circ}(\text{SnCl}_4, \text{g}, 298.15 \text{ K}) = (98.4 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{SnCl}_4, \text{g}, 298.15 \text{ K}) = (366.9 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

yielding:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{SnCl}_4, \text{g}, 298.15 \text{ K}) = - (439.6 \pm 3.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VIII.4.3 Gaseous bromides

### VIII.4.3.1 $\text{SnBr}_2(\text{g})$

Ideal gas properties of gaseous  $\text{SnBr}_2$  were calculated by [1991GUR/VEY] and [1963BRE/SOM] from spectroscopic and structural data. The data were those of [1958AKI/SPI], [1941LIS/SUT], [1983DEM/HER], [1983HAR/BLI], [1971HUB/OZII] and [1972OZI/VAN]. Gurvich and Veyts [1991GUR/VEY] re-evaluated the data and performed the calculations using the rigid rotator-harmonic oscillator approximation. Reported data are presented in Table VIII-24.

The standard enthalpy of formation of gaseous  $\text{SnBr}_2$  may be derived from data for the condensed phase compound. In Section VIII.1.3.1, the value

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = - (252.923 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$$

was selected. The enthalpy of sublimation may be deduced from vapour pressure measurements. The data sources are summarised in Table VIII-25. The enthalpy of sublimation was derived from these data with the use of evaluated auxiliary data for SnBr<sub>2</sub> [1991GUR/VEY].

Table VIII-24: Ideal gas properties of SnBr<sub>2</sub> from compilations/evaluations (C/E) and original articles (A).

Reference	$C_{p,m}^{\circ}$ (SnBr <sub>2</sub> , g, 298.15 K)/	$S_m^{\circ}$ (SnBr <sub>2</sub> , g, 298.15 K)/	$\Delta_f H_m^{\circ}$ (SnBr <sub>2</sub> , g 298.15 K)/
	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>
[1999BIN/MIL] <sup>(C/E)</sup>	55.17	335.8	- 103.9
[1963BRE/SOM] <sup>(C/E)</sup>	-	-	- 121
[1991GUR/VEY] <sup>(C/E)</sup>	56.39 <sup>(a)</sup>	329.041 <sup>(a)</sup>	- 118.3 ± 4.3 <sup>(a)</sup>
[2004KOL/REF] <sup>(A)</sup>	-	328.07	-
[1992BRU/WAL2] <sup>(A)</sup>	56.38	-	-

(a) Selected data.

Table VIII-25: Determination of the enthalpy of sublimation of SnBr<sub>2</sub> from vapour pressure measurements, neglecting dimerisation in the gas phase.

Reference	Method	T/K	Number of data	$\Delta_{\text{sub}} H_m^{\circ}$ (SnBr <sub>2</sub> , cr, 298.15 K)/kJ·mol <sup>-1</sup>	
				2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1939FIS/GEW]	Static	Boiling point, < 893 K	(a)	139.3 ± 2.2	135.1 ± 2.0
[1969KAR2]	Static	723-893	18	136.6 ± 1.8	134.2 ± 2.0
[1977TIT/STE]	Static	581-888	(a)	130	134.6 ± 2.0
[1992BRU/WAL]	Static	576-923	34	-	134.5 ± 3.0

(a) Data in equation form only.

The more accurate third law results were favoured and the selected value is

$$\Delta_{\text{sub}} H_m^{\circ} (\text{SnBr}_2, \text{cr}, 298.15 \text{ K}) = (134.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

Hence from these two data

$$\Delta_f H_m^{\circ} (\text{SnBr}_2, \text{g}, 298.15 \text{ K}) = - (118.3 \pm 4.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

Other selected data are

$$C_{p,m}^{\circ} (\text{SnBr}_2, \text{g}, 298.15 \text{ K}) = (56.4 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ} (\text{SnBr}_2, \text{g}, 298.15 \text{ K}) = (329.0 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^\circ(\text{SnBr}_2, \text{g}, 298.15 \text{ K}) = - (155.8 \pm 4.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

From mass spectrometric measurements on the vapour above liquid tin(II) bromide evidence was found for the existence of dimers  $\text{Sn}_2\text{Br}_4$  [1969KAR2]. This finding was corroborated later in more detailed measurements [1991HIL/MIL2], [1992BRU/WAL2]. Partial pressures of monomer and dimer in the vapour phase were determined by [1991HIL/MIL2] between 423 and 573 K. Their data, when extrapolated to 298 K, indicate that the mole fraction of dimers in the gas phase is approximately 0.01.

#### VIII.4.3.2 $\text{SnBr}_4(\text{g})$

Ideal gas properties of gaseous  $\text{SnBr}_4$  were calculated by [1962ANA] and [1991GUR/VEY] from spectroscopic and structural data. The data were those of [1941LIS/SUT], [1973DER/KOV], [1971CLA/RIP], [1972CLA/RIP], [1972CLA/RIP2], [1954DEL/FRA], [1977KON/MUL], [1971CLA/WIL], [1979CRE/SIN], [1976KON/MUL] and [1963MOS]. Gurvich and Veyts [1991GUR/VEY] re-evaluated the data and performed the calculations using the rigid rotator-harmonic oscillator approximation. Reported data appear in Table VIII-26.

Table VIII-26: Ideal gas properties of  $\text{SnBr}_4$  from compilations/evaluations (C/E) and original article (A).

Reference	$C_{p,m}^\circ(\text{SnBr}_4, \text{g}, 298.15 \text{ K})/$	$S_m^\circ(\text{SnBr}_4, \text{g}, 298.15 \text{ K})/$	$\Delta_f H_m^\circ(\text{SnBr}_4, \text{g}, 298.15 \text{ K})/$
	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
[1962ANA] <sup>(A)</sup>	103.4	412.6	-
[1991GUR/VEY] <sup>(C/E)</sup>	103.284 <sup>(a)</sup>	413.228 <sup>(a)</sup>	$-324.217 \pm 4.5$ <sup>(a)</sup>
[1973BAR/KNA] <sup>(C/E)</sup>	103.34	411.8	-314.6
[1993BAR] <sup>(C/E)</sup>	103.422	412.652	-348.109
[1999BIN/MIL] <sup>(C/E)</sup>	103.3	412.4	-347.6
[1982WAG/EVA] <sup>(C/E)</sup>	-	-	-314.6

(a) Selected data.

The standard enthalpy of formation of gaseous  $\text{SnBr}_4$  may be derived from data for the condensed phase compound. In Section VIII.1.3.2, the value

$$\Delta_f H_m^\circ(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = - (388.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

was selected. The enthalpy of sublimation may be deduced from vapour pressure measurements. Table VIII-27 summarises vapour pressure data sources. The enthalpy of sublimation was derived from these data, with the use of evaluated auxiliary data for

SnBr<sub>4</sub> [1991GUR/VEY]. The selected value was chosen from the more concordant data in Table VIII-27:

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{SnBr}_4, \text{cr}, 298.15 \text{ K}) = (63.8 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Hence from these two data

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnBr}_4, \text{g}, 298.15 \text{ K}) = - (324.2 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Table VIII-27: Enthalpy of sublimation of SnBr<sub>4</sub> as determined from vapour pressure measurements.

Reference	Method	<i>T</i> /K	Number of data	$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{SnBr}_4, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
				2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1951KAB/NYH]	Static	313-473	23	60.7 ± 1.1	63.4 ± 1.9
[1960KEA/SMI]	Static	280-301	12	62.5 ± 1.7	64.1 ± 1.0
[1960KEA/SMI]	Static	304-315	6	64.5 ± 1.9	64.0 ± 1.3
[1977TIT/STE]	Static	312-475	(a)	68.6	62.6 ± 2.0

(a) Data in equation form only.

Other selected data are

$$C_{p,m}^{\circ}(\text{SnBr}_4, \text{g}, 298.15 \text{ K}) = (103.3 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{SnBr}_4, \text{g}, 298.15 \text{ K}) = 413.2 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

which leads to:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{SnBr}_4, \text{g}, 298.15 \text{ K}) = - (341.4 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VIII.4.4 Gaseous iodides

### VIII.4.4.1 SnI<sub>2</sub>(g)

Ideal gas properties of gaseous SnI<sub>2</sub> were calculated by [1963BRE/SOM] and [1991GUR/VEY] from spectroscopic and structural data. The data were those of [1964CHA/DYA], [1983DEM/HER], [1958AKI/SPI], [1970BEA/PER] and [1969ZOL/FRO]. Gurvich and Veyts [1991GUR/VEY] re-evaluated the data and performed the calculations using the rigid rotator-harmonic oscillator approximation. Reported data appear in Table VIII-28.

The standard enthalpy of formation of gaseous SnI<sub>2</sub> may be derived from data for the condensed compound. The enthalpy of sublimation of the solid may be derived from vapour pressure measurements; Table VIII-29 summarises data sources. The same property was determined by other methods (Table VIII-30). The enthalpy of

sublimation was deduced from vapour pressure data with the use of evaluated auxiliary data for SnI<sub>2</sub> [1991GUR/VEY].

Table VIII-28: Ideal gas properties of SnI<sub>2</sub> from compilations/evaluations, neglecting dimerisation in the gas phase.

Reference	$C_{p,m}^{\circ}$ (SnI <sub>2</sub> , g, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}$ (SnI <sub>2</sub> , g, 298.15 K)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta_f H_m^{\circ}$ (SnI <sub>2</sub> , g, 298.15 K)/ kJ·mol <sup>-1</sup>
[1963BRE/SOM]	-	-	8.4
[1991GUR/VEY]	56.744 <sup>(a)</sup>	342.702 <sup>(b)</sup>	- 8.067 <sup>(a)</sup>
[1993BAR]	56.437	343.289	- 3.084
[1999BIN/MIL]	56.74	343.2	- 0.9

(a) Selected data

Table VIII-29: The enthalpy of sublimation of SnI<sub>2</sub> as derived from vapour pressure measurements.

Reference	Method	T/K	Number of data	$\Delta_{\text{sub}} H_m^{\circ}$ (SnI <sub>2</sub> , cr, 298.15 K)/kJ·mol <sup>-1</sup>	
				2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1939FIS/GEW2]	Static	711-956	12	144.9 ± 2.5	144.4 ± 2.8
[1967KAR3]	Static	773-973	11	140.4 ± 1.5	144.8 ± 3.1
[1973VOR/VOR]	Static	780-960	a	144.1	145.2 ± 2.5
[1977ZHA/TIT3], [1978ZHA/TIT2]	Static	596-963	a	172	-

(a) Data in equation form only.

Table VIII-30: The enthalpy of sublimation of SnI<sub>2</sub> as determined by other methods.

Reference	Method	$\Delta_{\text{sub}} H_m^{\circ}$ (SnI <sub>2</sub> , cr, 298.15 K)/kJ·mol <sup>-1</sup>	
		2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1981HIR/KLE]	Mass spectrometric	171.9	-
[1982MUR/IVA]	Spectrophotometric	135.9	-
[1985HIL/BEN]	Mass spectrometric	148.7 ± 3.0	141.4 ± 1.4

The selected value

$$\Delta_{\text{sub}} H_m^{\circ} (\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = (144.9 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$$

was chosen from the more concordant data in Table VIII-29 and Table VIII-30. In Section VIII.1.4.2, the value



$$\Delta_f H_m^\circ (\text{SnI}_2, \text{cr}, 298.15 \text{ K}) = - (153.0 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

was selected. Hence from these two data

$$\Delta_f H_m^\circ (\text{SnI}_2, \text{g}, 298.15 \text{ K}) = - (8.1 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

Other selected data are

$$C_{p,m}^\circ (\text{SnI}_2, \text{g}, 298.15 \text{ K}) = (56.7 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ (\text{SnI}_2, \text{g}, 298.15 \text{ K}) = (342.7 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection leads to:

$$\Delta_f G_m^\circ (\text{SnI}_2, \text{g}, 298.15 \text{ K}) = - (60.4 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

From mass spectrometric measurements of the vapour over liquid  $\text{SnI}_2$  at 793 to 953 K [1967KAR3], evidence was found for the existence of the dimer  $\text{Sn}_2\text{I}_4$ . This was corroborated by Knudsen effusion/mass spectrometric measurements [1985HIL/BEN] at 474 to 582 K. From temperature-dependent relative abundances of monomer and dimer [1985HIL/BEN], it is estimated that the mole fraction of dimers in the gas phase at 298 K is  $\ll 0.01$ . The less accurate measurements of [1967KAR3] qualitatively agree with this conclusion.

#### VIII.4.4.2 $\text{SnI}_4(\text{g})$

Ideal gas properties of gaseous  $\text{SnI}_4$  were calculated by [1962ANA] and [1991GUR/VEY] from spectroscopic and structural data. Data sources are given in Table VIII-31.

Table VIII-31: Data sources for the calculation of ideal gas properties of  $\text{SnI}_4$ .

Data type	References
Electron diffraction	[1941LIS/SUT]
Spectroscopic	[1971CLA/RIP], [1972CLA/RIP], [1972CLA/RIP2], [1952DEL/BUI], [1974VOR/DER], [1964BUT/GER], [1976CAR/WOO], [1980CLA/DIN], [1974CLA/MIT], [1971CLA/WIL], [1975DAW], [1962GER/HAD], [1968HAD/DEC], [1973KAM/MAE], [1970KIE/SCH], [1956STA/FOR]

The data were re-evaluated by [1991GUR/VEY], who performed the calculations using the rigid rotator-harmonic oscillator approximation. Reported data are presented in Table VIII-32.

The standard enthalpy of formation of gaseous  $\text{SnI}_4$  may be derived from data for the condensed compound. In Section VIII.1.4.3, the value

$$\Delta_f H_m^\circ (\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = - (207.45 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$$

was selected. The enthalpy of sublimation may be deduced from vapour pressure measurements. Table VIII-33 summarises data sources. The enthalpy of sublimation was deduced from these data with the use of evaluated auxiliary data for SnI<sub>4</sub> [1991GUR/VEY]. The selected value was chosen from the more concordant results in Table VIII-33:

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = (88.6 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

Table VIII-32: Ideal gas properties of SnI<sub>4</sub> from compilation/evaluations (C/E) and original article (A).

Reference	$C_{p,m}^{\circ}(\text{SnI}_4, \text{g}, 298.15 \text{ K})/$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_{\text{m}}^{\circ}(\text{SnI}_4, \text{g}, 298.15 \text{ K})/$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_{\text{r}}H_{\text{m}}^{\circ}(\text{SnI}_4, \text{g}, 298.15 \text{ K})/$ $\text{kJ}\cdot\text{mol}^{-1}$
[1962ANA] <sup>(A)</sup>	105.3	446.3	-
[1991GUR/VEY] <sup>(C/E)</sup>	105.467 <sup>(a)</sup>	448.730 <sup>(a)</sup>	- 118.854 <sup>(a)</sup>
[1993BAR] <sup>(C/E)</sup>	105.313	446.375	- 127.696
[1999BIN/MIL] <sup>(C/E)</sup>	105.1	446.4	- 118
[1982WAG/EVA] <sup>(C/E)</sup>	105.4	446.1	-

(a) Selected data

Table VIII-33: Enthalpy of sublimation of SnI<sub>4</sub> as derived from vapour pressure measurements.

Reference	Method	$T/\text{K}$	Number of data	$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{SnI}_4, \text{cr}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
				2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1936NEG]	Static	433-524	6	82.9 ± 1.8	88.3 ± 2.6
[1941SEK]	Static	365-414	a	78.0	87.8 ± 3.0
[1941SEK]	Static	419-449	a	86.7	88.6 ± 2.6
[1951KAB/NYH]	Static	422-611	19	85.0 ± 1.8	88.4 ± 3.0
[1978TIT/ZHA]	Static	359-416	(a)	90.4	89.0 ± 2.2
[1977ZHA/TIT]	Static	420-562	(a)	89.4	88.9 ± 3.0

(a) Data in equation form only.

Hence from these two data

$$\Delta_f H_m^\circ (\text{SnI}_4, \text{g}, 298.15 \text{ K}) = - (118.9 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

Other selected data are

$$C_{p,m}^\circ (\text{SnI}_4, \text{g}, 298.15 \text{ K}) = (105.5 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ (\text{SnI}_4, \text{g}, 298.15 \text{ K}) = (448.7 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

which yields:

$$\Delta_f G_m^\circ (\text{SnI}_4, \text{g}, 298.15 \text{ K}) = - (168.2 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$



# Chapter IX

## Group 16 compounds and complexes

### IX.1 Sulfur compounds and complexes

#### IX.1.1 Tin sulfides

##### IX.1.1.1 Aqueous sulfido complexes of tin(IV)

Stannic sulfide is soluble in Na<sub>2</sub>S or (NH<sub>4</sub>)<sub>2</sub>S solutions forming the thioannate ion (Reaction (IX.1)):



Only two (three?) experimental studies on the above equilibrium are available so far [1956BAB/LIS], [1968HSE/REC]. In both papers, the calculation was based on a much lower protonation constant of the sulfide ion (see footnote in Table IX-1) than currently accepted ( $\log_{10} K = (19.0 \pm 2.0)$ ). Therefore, although the reported equilibrium constants agree well with each other (Table IX-1), the true value is probably several orders of magnitude higher. The re-evaluation of the experimental data reported in [1956BAB/LIS] and [1968HSE/REC] resulted in considerably higher equilibrium constants indeed (see Appendix A).

Table IX-1: Experimental equilibrium constants for sulfido complexes of tin(IV).

Method	Ionic media	<i>t</i> /°C	$\log_{10} K$ reported	$\log_{10} K$ recalculated <sup>(a)</sup>	Reference
$\text{SnS}_2(\text{s}) + \text{S}^{2-} \rightleftharpoons \text{SnS}_3^{2-}$					
sol	?	20	5.04 <sup>(b)</sup>	9.1 ± 2.0	[1956BAB/LIS]
Ise-S <sup>2-</sup>	0.1 M NaNO <sub>3</sub>	25	5.31 ± 0.02 <sup>(c)</sup>	9.2 ± 2.0	[1968HSE/REC]
$\text{SnS}_2(\text{s}) + \text{HS}^- \rightleftharpoons \text{SnS}_3^{2-} + \text{H}^+$					
sol	?	20		-9.9 ± 1.0	[1956BAB/LIS]

(a) Re-evaluated values (see Appendix A).

(b) The first protonation constant used by the authors is  $\log_{10} K_1 = 14.92$ .

(c) The first protonation constant used by the authors is  $\log_{10} K_1 = 14.44$ .

Owing to the high uncertainty of the first protonation constant of sulfide ion, Eq. (IX.2) is thermodynamically better defined than Eq. (IX.1).



Only in [1956BAB/LIS] appropriate data to determine the equilibrium constant for the above reaction (see Table IX-1) are reported. Due to the reasons mentioned in Appendix A thermodynamic equilibrium constants cannot be selected based on these reports, but the recalculated values can be used until more data will be published on this system.

### IX.1.1.2 Solid tin sulfides

#### IX.1.1.2.1 General considerations

Phase diagram and thermodynamic data pertinent to the S-Sn system were reviewed and evaluated critically by [1986SHA/CHA]. This review is particularly useful for establishing the number and identity of stoichiometric tin sulfides, as well as their melting and transition properties and temperature stability. Cruz *et al.* [2003CRU/MOR] synthesised tin sulfides by direct reaction of the elements, followed by XRD analysis of the products. Their results, concerning the identity of stoichiometric tin sulfides, agree with those of [1986SHA/CHA]. Thermodynamic data of tin sulfides reported up to 1974 were reviewed and critically evaluated by [1974MIL]; later data were also considered similarly by [1991GUR/VEY]. These publications constituted a guide to relevant data sources and aid in the choice of selected data from original papers.

#### IX.1.1.2.2 SnS(cr)

Solid SnS exists in two forms. The low temperature form (orthorhombic,  $\alpha$ -SnS) transforms to the high temperature form (cubic,  $\beta$ -SnS) at  $(875 \pm 10)$  K [1986SHA/CHA], [1991GUR/VEY]. (Unless otherwise stated, uncertainties are those of the original experimenter/evaluator.)  $\beta$ -SnS melts congruently at  $(1154 \pm 2)$  K [1991GUR/VEY].

The heat capacity of solid SnS was measured by adiabatic calorimetry (52 to 298 K) [1953KIN/TOD], by drop calorimetry (388 to 1144 K) [1958ORR/CHR]; (300 to 857 K) [1974BLA/IGE], (288 to 973 K) [1936KRE/FEI] and by light-pulse heating (200 to 800 K), [1968FEI/NAZ]. The data of [1968FEI/NAZ] are given only as points on a graph, which were read off the graph and included in Table IX-2. The data of [1968FEI/NAZ] deviate significantly from the other data sources and are not considered further. The data of [1936KRE/FEI] were reported only as average values over various temperature ranges. Table IX-3 presents the parameters of curve-fitting equations for  $C_{p,m}^{\circ}$  (SnS, cr,  $T$ ) for specific temperature ranges. The unconventional equation used by Wiedemeier *et al.* fits to the heat-capacity data over the temperature range

$100 \leq T/K \leq 875$ , see Table IX-3 and Figure IX-1. The selected data [1991GUR/VEY] are based on those of [1958ORR/CHR] and [1953KIN/TOD].

Table IX-2: The heat capacity of  $\alpha$ -SnS as measured (M) and evaluated (E).

$T/K$	$C_{p,m}^{\circ}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$				
	[1974BLA/IGE] (M)	[1993BAR] (E)	[1973BAR/KNA] (E)	[1968FEI/NAZ]	[1991GUR/VEY2] (E)
298.15		49.257	49.258		49.2
300	49.01	49.262	49.262	49.7	48.8
350	50.25				49.2
400	51.49	50.562	50.559	54.0	51.1
450	52.73				51.6
500	53.97	52.844	52.844	55.4	52.3
550	55.21				53.4
600	56.45	55.513	55.513		55.1

The numbers of significant figures are those of the original experimenter/evaluator.

Table IX-3: The heat capacity of  $\alpha$ -SnS as represented by fitting equations of the type:

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/K) + c [\ln(T/K)]^2 + d [\ln(T/K)]^3\} \quad \text{Ref. (1)}$$

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/K + c (T/K)^{-2} \quad \text{Refs. (2)}$$

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/K \quad \text{Ref. (3)}$$

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a. \quad \text{Ref. (3)}$$

Refs.	$T/K$	$a$	$b$	$c$	$d$
(1)	100 – 875	-19.1440	11.6659	-1.99273	0.114905
(2)	298 – 875	35.7	$3.13 \times 10^{-2}$	$3.76 \times 10^{-5}$	
(3)	875 – 1153	35.69	$7.48 \times 10^{-3}$		
(3)	1153 – 1250	74.89			

References: (1): [1980WIE/CSI2] (2): [1958ORR/CHR], [1960KEL], [1973BAR/KNA], and [1999BIN/MIL]; (3): [1958ORR/CHR].

A value for the standard entropy was derived from mass spectrometric measurements [1979WIE/CSI]. The low temperature heat-capacity measurements of [1953KIN/TOD] were chosen by [1974MIL], [1991GUR/VEY] for the determination of  $S_m^{\circ}(\text{SnS}, \text{cr}, 298.15 \text{ K})$ . Re-evaluation of the heat-capacity data of King and Todd by these reviewers essentially confirmed their entropy value which was selected, see

Appendix A entry on [1953KIN/TOD]. A summary of evaluated data is given in Table IX-4.

Figure IX-1: Heat capacity function of  $\alpha$ -SnS.

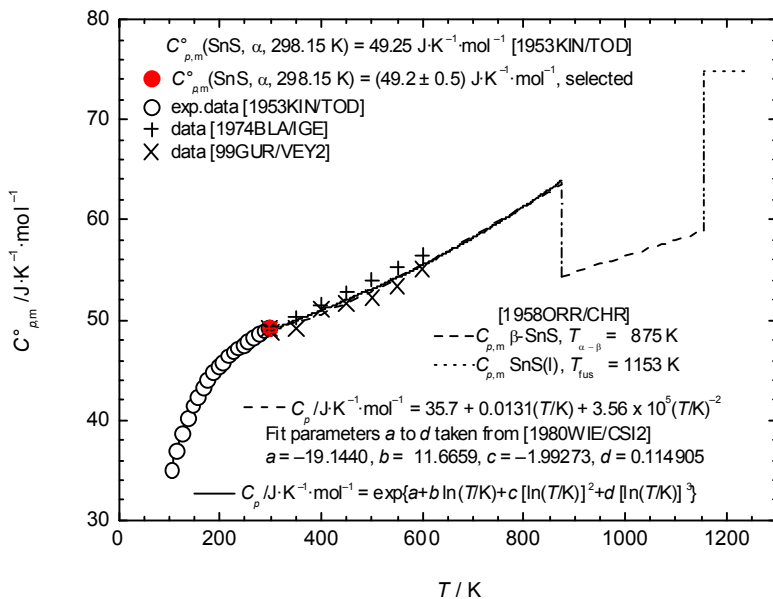


Table IX-4: The standard entropy of  $\alpha$ -SnS, as reported from measurement and evaluation/compilation.

Reference	Type of report	$S_m^\circ$ (SnS, $\alpha$ , 298.15 K)/ $J \cdot K^{-1} \cdot mol^{-1}$
[1979WIE/CSI]	Experimental Knudsen effusion/mass spectrometry	$79.9 \pm 6.0$
[1953KIN/TOD], [1991GUR/VEY]	Experimental low temperature $C_p$	$77.000^*$
[1982WAG/EVA], [1973BAR/KNA], [1995ROB/HEM], [1999BIN/MIL]	Evaluation/compilation	77.0
[1952ROS/WAG]	Evaluation/compilation	98.7
[1978ROB/HEM]	Evaluation/compilation	$76.82 \pm 0.84$
[1993BAR], [1964HIR]	Evaluation/compilation	76.986

\* Value selected in the present evaluation.



Data for the determination of  $\Delta_f H_m^\circ$  (SnS,  $\alpha$ , 298.15 K) were obtained by the transpiration method (measurements on SnS + H<sub>2</sub> mixtures), cell-potential measurements, mass spectrometry or by calorimetry (heat of reaction of SnS with Zn). The results are summarised in Table IX-5. Table IX-6 contains values quoted in compilations/evaluations. In Table IX-5, the uncertainties given for results from the transpiration method reflect only the reproducibility of the data. Uncertainties in the data used for  $\Delta_f H_m^\circ$  (H<sub>2</sub>S, g, 298.15 K) and the necessary data for  $\alpha$ -SnS are approximately 1.4 kJ·mol<sup>-1</sup>. The selected value of  $\Delta_f H_m^\circ$  (SnS,  $\alpha$ , 298.15 K) is based on the data of [1951SUD], [1955RIC], [1965RAU], [1966ESP] and [1973MOR/STO].

Table IX-5: Experimental determination of the standard enthalpy of formation of  $\alpha$ -SnS after [1991GUR/VEY].

Reference	Method	$\Delta_f H_m^\circ$ (SnS, $\alpha$ , 298.15 K)/kJ·mol <sup>-1</sup>	
		Second law	Third law
[1925JEL/ZAK]	Transpiration		- 102.1 ± 10.0
[1930BRI/KAP]	Transpiration		- 91.1 ± 2.3
[1934BRI/KAP]	Transpiration	- 77.0 ± 25.0	- 96.8 ± 2.3
[1938KAP/MAK]	Cell potential		- 84.8 ± 1.0
[1951SUD]	Transpiration	- 89.0 ± 25.0	- 107.8 ± 2.3
[1955RIC]	Transpiration	- 106.9 ± 7.0	- 106.3 ± 0.4
[1965RAU]	Transpiration		- 109.0 ± 0.2
[1966ESP]	Transpiration	- 111.9 ± 0.2	- 107.6 ± 0.4
[1973MOR/STO], [1973MOR/STO2]	Calorimetry		- 111.0 ± 5.0
[1979WIE/CSI]	Mass spectrometry		- 102.9 ± 4.0
[1984FRE/ROS]	Cell potential	- 87.0 ± 4.0	- 100.4 ± 0.6
[1984FRE/ROS]	Transpiration		- 110.2 ± 0.3

Table IX-6: The standard enthalpy of formation of  $\alpha$ -SnS as quoted in compilations/evaluations.

Reference	$\Delta_f H_m^\circ$ (SnS, $\alpha$ , 298.15 K)/kJ·mol <sup>-1</sup>
[1993BAR]	- 107.947
[1978ROB/HEM], [1995ROB/HEM]	- 106.541 ± 1.464
[1973BAR/KNA], [1999BIN/MIL]	- 108.0
[1952ROS/WAG]	- 77.8
[1982WAG/EVA]	- 100.0
[1991GUR/VEY]	- 109.622 ± 4.000*
[1974MIL]	- 108.0 ± 2.0

\* Value selected by this review.

The heat capacity of  $\alpha$ -SnS is generated by the equation from Table IX-3:

$$[C_{p,m}^{\circ}]_{100\text{K}}^{875\text{K}}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.3})$$

where  $a = -19.1440$ ,  $b = 11.6659$ ,  $c = -1.99273$  and  $d = 0.114905$  [1980WIE/CSI2].

The standard deviation of  $C_{p,m}^{\circ}$  is  $\pm 0.24 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The following values were selected. The heat capacity of  $\alpha$ -SnS is:

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K}) = (49.2 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

the standard entropy is:

$$S_{\text{m}}^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K}) = (76.82 \pm 0.84) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the standard enthalpy of formation is:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K}) = -(109.6 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K}) = -(107.7 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

### IX.1.1.2.3 $\text{Sn}_2\text{S}_3(\text{cr})$

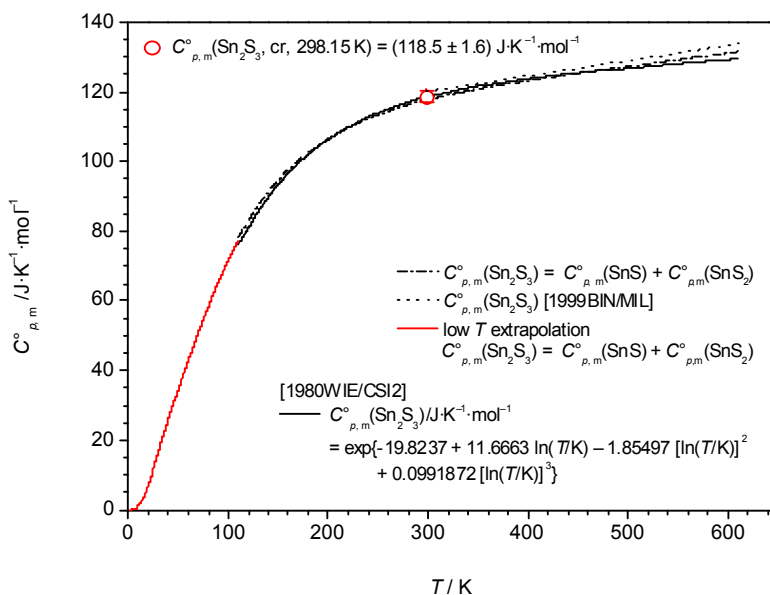
This solid compound reportedly [1969MOH] exists in four modifications, with transition temperatures 948, 988 and 1017 K. It melts peritectically at 1033 K [1969MOH].

The heat capacity was measured in the range of 110 to 610 K by DSC [1980WIE/CSI2]. The data were fitted to the equation

$$[C_{p,m}^{\circ}]_{100\text{K}}^{610\text{K}}(\text{Sn}_2\text{S}_3, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.4})$$

where  $a = -19.8237$ ,  $b = 11.6663$ ,  $c = -1.85497$  and  $d = 0.0991872$  [1980WIE/CSI2].

In the temperature range 100 to 610 K the relationship  $C_{p,m}^{\circ}(\text{Sn}_2\text{S}_3) = C_{p,m}^{\circ}(\text{SnS}, \alpha) + C_{p,m}^{\circ}(\text{SnS}_2)$  is accurate within  $\pm 2 \%$ . In view of the bonding and structural similarities of these compounds, the agreement with Neumann-Kopp's rule [1831NEU], [1864KOP] was expected and extended to the temperature range 0 to 100 K, see Figure IX-2. Equation (IX.4) reproduces the data within a standard error of estimate of  $\pm 0.78 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The equation  $C_{p,m}^{\circ}(\text{Sn}_2\text{S}_3, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 107.03 + 43.93 \times 10^{-3} T/\text{K}$  [1999BIN/MIL] (no source stated, no uncertainty stated) is less well established than Eq. (IX.4) and has not been taken into account.

Figure IX-2: Heat capacity function of  $\text{Sn}_2\text{S}_3(\text{cr})$ .

Wiedemeier and Csillag [1980WIE/CSI2] used their  $C_{p,m}^{\circ}$  data below 298 K to deduce a value for the standard entropy of this compound. The same authors also used Knudsen effusion/mass spectrometry [1980WIE/CSI3]. Rau [1965RAU] used decomposition/sublimation pressure measurements on  $\text{Sn}_2\text{S}_3$ . The experimental results are collected in Table IX-7.

Table IX-7: Experimental measurements of the standard entropy of  $\text{Sn}_2\text{S}_3(\text{cr})$  and data from compilations/evaluations.

Reference	Method	$S_m^{\circ}(\text{Sn}_2\text{S}_3, \alpha, 298.15 \text{ K}) / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Experimental measurements		
[1965RAU]	Decomposition/sublimation pressure	$132.2 \pm 15.0$
[1980WIE/CSI2]*	Low temperature heat capacity	$163.6 \pm 6.0$
[1980WIE/CSI3]	Knudsen effusion/mass spectrometry	$170.5 \pm 6.0$
Compilations/evaluations		
[1977BAR/KNA]		164.0
[1974MIL], [1999BIN/MIL]		164.4

\* Value selected by this review.

Data for  $\Delta_f H_m^\circ$  ( $\text{Sn}_2\text{S}_3$ , cr, 298.15 K) were obtained by reaction calorimetry [1973STO/NEK] and by Knudsen effusion/mass spectrometry ([1980WIE/CSI3] and [1991PIA/FOG]). The data are presented in Table IX-8. The datum of [1973STO/NEK] is questionable because auxiliary information was lacking and possible sources of error were not addressed (editor's comments in [1973STO/NEK2]). Rau [1965RAU] measured decomposition/sublimation pressures of  $\text{SnS}$ , as did [1937GER/KRU] and [1967KAR/PAS]. Data from compilations/evaluations are also given in Table IX-8.

Table IX-8: Experimental determination of the standard enthalpy of formation of  $\text{Sn}_2\text{S}_3(\text{cr})$  and data from compilations/evaluations.

Experimental measurements		
Reference	Method	$\Delta_f H_m^\circ$ ( $\text{Sn}_2\text{S}_3$ , cr, 298.15 K)/kJ·mol <sup>-1</sup>
[1973STO/NEK]	Reaction calorimetry	- 266.0 ± 4.0
[1980WIE/CSI3]	Knudsen effusion/mass spectrometry	- 254.5 ± 6.0
[1991PIA/FOG]	Knudsen effusion/mass spectrometry	- 253.0 ± 2.0
[1937GER/KRU]	Dissociation pressure	- 264.0 ± 21.0 (3 <sup>rd</sup> law)
[1967KAR/PAS]	Dissociation pressure	- 239.0 ± 29.0 (2 <sup>nd</sup> law)
		- 263.0 ± 21.0 (3 <sup>rd</sup> law)
[1965RAU]	Decomposition/sublimation pressure	- 297.5 ± 11.0
[1957SEV]	Dissociation pressure	- 270.1 ± 6.0
Compilations/evaluations		
Reference		$\Delta_f H_m^\circ$ ( $\text{Sn}_2\text{S}_3$ , cr, 298.15 K)/kJ·mol <sup>-1</sup>
[1974MIL]		- 264.0 ± 21.0*
[1993BAR]		- 263.592
[1999BIN/MIL]		- 263.6
[1977BAR/KNA]		- 263.0

\* Value selected by this review.

The selected heat capacity of  $\text{Sn}_2\text{S}_3(\text{cr})$  is given by Eq. (IX.4), with the standard error of estimate in  $C_{p,m}^\circ = \pm 1.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,

$$C_{p,m}^\circ (\text{Sn}_2\text{S}_3, \text{cr}, 298.15 \text{ K}) = (118.5 \pm 1.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The selected standard entropy of  $\text{Sn}_2\text{S}_3$  is

$$S_m^\circ (\text{Sn}_2\text{S}_3, \text{cr}, 298.15 \text{ K}) = (163.6 \pm 6.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the selected standard enthalpy of formation is

$$\Delta_f H_m^\circ (\text{Sn}_2\text{S}_3, \text{cr}, 298.15 \text{ K}) = - (264.0 \pm 21.0) \text{ kJ}\cdot\text{mol}^{-1},$$

which yields:

$$\Delta_f G_m^\circ (\text{Sn}_2\text{S}_3, \text{cr}, 298.15 \text{ K}) = - (253.6 \pm 21.1) \text{ kJ}\cdot\text{mol}^{-1},$$

**IX.1.1.2.4 SnS<sub>2</sub>(cr)**

This compound melts congruently at  $(1143 \pm 15)$  K [1986SHA/CHA], [1991GUR/VEY].

The heat capacity was measured by adiabatic calorimetry at 53 to 298 K [1953KIN/TOD] and at 400 to 1005 K by drop calorimetry [1958ORR/CHR]. The parameters of some curve-fitting equations, using these data, are given in Table IX-9.

Table IX-9: The heat capacity of SnS<sub>2</sub>(cr) as given by curve-fitting equations of the type:

$$C_{p,m}^{\circ}(\text{SnS}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad \text{Ref. (1)}$$

$$C_{p,m}^{\circ}(\text{SnS}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/\text{K} \quad \text{Ref. (2)}$$

$$C_{p,m}^{\circ}(\text{SnS}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T/\text{K} + c (T/\text{K})^{-2}. \quad \text{Ref. (3)}$$

Refs.	<i>T</i> /K	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
(1)	100 – 1005	– 23.6488	13.2230	– 2.10132	0.112224
(2)	298 – 1000	64.89	$1.757 \times 10^{-2}$		
(3)	298 – 1000	64.91	$1.756 \times 10^{-3}$	$- 1.483 \times 10^3$	

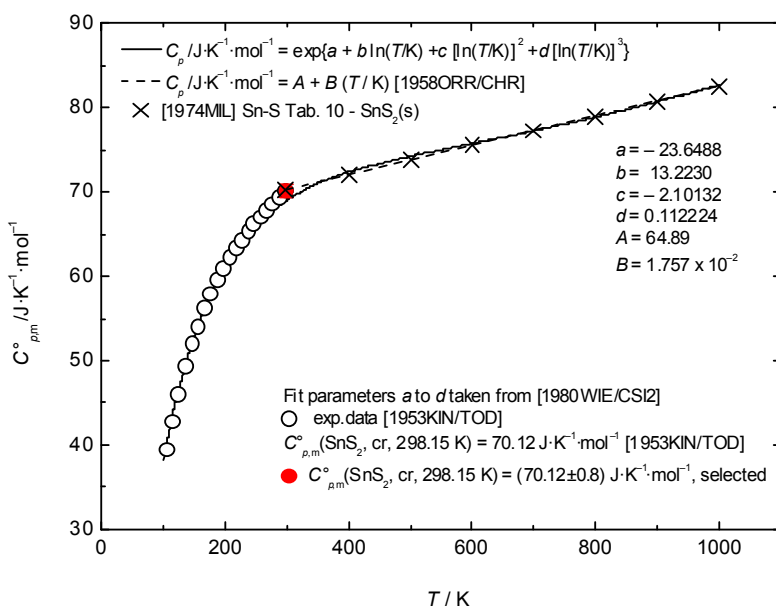
References: (1): [1980WIE/CSI] (2): [1958ORR/CHR]; (3): [1974MIL].

Comparisons with experimental data are given in Table IX-10 and Figure IX-3.

Table IX-10: Heat capacity of SnS<sub>2</sub>(cr). Comparison of experimental and fitting equation data.

<i>T</i> /K	$C_{p,m}^{\circ}(\text{SnS}_2, \text{cr}, 298.15 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		
	Experiment	Fitted	
		[1953KIN/TOD], [1958ORR/CHR]	[1978ROB/HEM], [1995ROB/HEM]
298.15	70.12	70.12	68.92
300	70.16	70.17	69.01
400	71.92	72.05	72.31
500	73.98	73.52	74.20
600	75.43	75.19	75.70

The low temperature heat-capacity data of [1953KIN/TOD] were used to derive the standard entropy of SnS<sub>2</sub> by [1953KIN/TOD] and [1980WIE/CSI2]. The values, with other data from compilations, are given in Table IX-11. The data were fitted in the present review.

Figure IX-3: Heat capacity function of SnS<sub>2</sub>(cr).Table IX-11: The standard entropy of SnS<sub>2</sub>(cr) from measurement (M) and quoted in compilations/evaluations (E).

Reference	$S_m^\circ$ (SnS <sub>2</sub> , cr, 298.15 K)/J·K <sup>-1</sup> ·mol <sup>-1</sup>
[1953KIN/TOD] (M), [1974MIL], [1977BAR/KNA] (E)	87.5 ± 0.8
[1980WIE/CSI] (M)	87.1 ± 4.0
[1980WIE/CSI2] (E)	87.59
[1991GUR/VEY] (E), [1999BIN/MIL] (E)	87.400 ± 1.500*
[1978ROB/HEM], [1995ROB/HEM](E)	87.5 ± 0.2
[1993BAR](E)	87.446
[1982WAG/EVA](E)	87.4

\* Value selected by this review.

The overall scatter in the data for the standard enthalpy of formation of SnS<sub>2</sub> of Table IX-12 is unacceptably large. The datum of [1973MOR/STO], from calorimetry, is considered here to be an outlier to all the other data, derived from gas equilibrium experiments. The report [1973MOR/STO] is only an abstract, providing few details. The complete report [1973MOR/STO2] is an inaccessible VINITI document. In view of this anomalous datum and lack of experimental details, the result of [1973MOR/STO] is excluded from further consideration.

Table IX-12: Experimental determination of the standard enthalpy of formation of SnS<sub>2</sub>(cr) after [1991GUR/VEY].

Reference	Method	T/K	data points/ experiments	$\Delta_f H_m^\circ$ (SnS <sub>2</sub> , cr, 298.15 K)/ kJ·mol <sup>-1</sup>	
				Second law	Third law
[1937GER/KRU]	Static 2 SnS <sub>2</sub> (cr) $\rightleftharpoons$ Sn <sub>2</sub> S <sub>3</sub> (cr) + ½ S <sub>2</sub> (g)	923 – 973	3	- 148 ± 13	- 161 ± 13
[1957SEV]	Transpiration 2 SnS <sub>2</sub> (cr) + H <sub>2</sub> (g) $\rightleftharpoons$ Sn <sub>2</sub> S <sub>3</sub> (cr) + H <sub>2</sub> S(g)	623 – 773	4	- 178 ± 17	- 172 ± 12
[1967KAR/PAS]	Static SnS <sub>2</sub> (cr) $\rightleftharpoons$ products <sup>(a)</sup>	773 – 1020	9		- 160 ± 14
[1980WIE/CSI]	Knudsen effusion	678 – 820		- 154.6 ± 4.0	- 157.5 ± 4.0
[1980WIE/CSI3]	2 SnS <sub>2</sub> (cr) $\rightleftharpoons$ 2 SnS(cr) + S <sub>2</sub> (g) <sup>(b)</sup>				
[1973MOR/STO]	Calorimetry 2 SnS <sub>2</sub> (cr) + 4 Zn(cr) $\rightleftharpoons$ 2 Sn(cr) + 4 ZnS(cr)	?	8	- 123.0 ± 10.0	
[1991PIA/FOG]	Knudsen effusion 2 SnS <sub>2</sub> (cr) $\rightleftharpoons$ 2 SnS(cr) + S <sub>2</sub> (g)	689 – 807	28		- 148 ± 2

(a) The reaction scheme used by [1967KAR/PAS] was: 4 SnS<sub>2</sub>(cr)  $\rightleftharpoons$  2 Sn<sub>2</sub>S<sub>3</sub>(cr) + S<sub>2</sub>(g); 6 Sn<sub>2</sub>S<sub>3</sub>(cr)  $\rightleftharpoons$  4 Sn<sub>3</sub>S<sub>4</sub>(cr) + S<sub>2</sub>(g); 2 Sn<sub>3</sub>S<sub>4</sub>(cr)  $\rightleftharpoons$  6 SnS(cr) + S<sub>2</sub>(g).

(b) The equilibrium constants used in calculation were obtained by combination of those for the following reactions: 2 SnS<sub>2</sub>(cr)  $\rightleftharpoons$  Sn<sub>2</sub>S<sub>3</sub>(cr) + ½ S<sub>2</sub>(g), 678 – 798 K, 42 points; Sn<sub>2</sub>S<sub>3</sub>(cr)  $\rightleftharpoons$  2 SnS(cr) + ½ S<sub>2</sub>(g), 677 – 820 K, 48 points.

[1991GUR/VEY] recalculated the enthalpy of formation using the original raw data of [1937GER/KRU], [1957SEV], [1967KAR/PAS], [1980WIE/CSI] and [1973MOR/STO]. They used a consistent set of auxiliary data for the thermodynamic properties of SnS(cr), Sn<sub>2</sub>S<sub>3</sub>(cr), H<sub>2</sub>S(g), S<sub>2</sub>(g) and ZnS(cr). The imputed compounds Sn<sub>3</sub>S<sub>4</sub> and Sn<sub>4</sub>S<sub>5</sub>, used by some investigators, were not considered. The only data not consistently treated were those of [1991PIA/FOG], since these appeared too late to be considered by [1991GUR/VEY].

In their evaluation, [1991GUR/VEY] opted to combine both calorimetric and gas-phase equilibrium data and gave as their recommended datum:  $\Delta_f H_m^\circ$  (SnS<sub>2</sub>, cr, 298.15 K) = - (142 ± 15) kJ·mol<sup>-1</sup>.

Since the present evaluation dispenses with the calorimetric datum, the selected value will be more negative (Table IX-13).

Table IX-13: Evaluated/compiled values for the standard enthalpy of formation of SnS<sub>2</sub>(cr).

Reference	$\Delta_f H_m^\circ$ (SnS <sub>2</sub> , cr, 298.15 K)/kJ·mol <sup>-1</sup>
[1991GUR/VEY]	- 142 ± 15
[1974MIL], [1977BAR/KNA]	- 154
[1978ROB/HEM], [1995ROB/HEM]	- 149.8 ± 5.0
[1993BAR], [1999BIN/MIL]	- 153.553

The required selected datum for the enthalpy of formation may therefore be deduced from all the data derived from gas-equilibrium experiments in Table IX-12. This datum is:

$$\Delta_f H_m^\circ (\text{SnS}_2, \text{cr}, 298.15 \text{ K}) = - (151.5 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

While the standard deviation of 1.6 kJ·mol<sup>-1</sup> is statistically correct, an uncertainty of ± 4 kJ·mol<sup>-1</sup> has been considered to be more realistic.

The heat capacity of SnS<sub>2</sub>(cr) is generated by Eq. (IX.5):

$$[C_{p,m}^\circ]_{100\text{K}}^{1005\text{K}} (\text{SnS}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.5})$$

where  $a = -23.6488$ ,  $b = 13.2230$ ,  $c = -2.10132$  and  $d = 0.112224$  [1980WIE/CSI2], and the standard deviation of the heat-capacity data [1953KIN/TOD], [1958ORR/CHR] is ± 0.38 J·K<sup>-1</sup>·mol<sup>-1</sup>.

The selected heat capacity is:

$$C_{p,m}^\circ (\text{SnS}_2, \text{cr}, 298.15 \text{ K}) = (70.12 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The selected standard entropy is:

$$S_m^\circ (\text{SnS}_2, \text{cr}, 298.15 \text{ K}) = (87.400 \pm 1.500) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the selected standard enthalpy of formation is:

$$\Delta_f H_m^\circ (\text{SnS}_2, \text{cr}, 298.15 \text{ K}) = - (151.5 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection leads to:

$$\Delta_f G_m^\circ (\text{SnS}_2, \text{cr}, 298.15 \text{ K}) = - (143.2 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### IX.1.1.2.5 Sn<sub>3</sub>S<sub>4</sub>(cr)

Mills [1974MIL] treats this as a stable stoichiometric compound, citing a (peritectic) melting point of 983 K. The phase diagram of [1966KAR/PAS] shows this; however, it is absent in the careful work of [1961ALB/SCH], [1962MOH] and [1969MOH]. The XRD results [1966KAR/PAS] were interpreted to indicate a tetragonal structure. Both [1967KAR/PAS] and [1937GER/KRU] derived standard enthalpy of formation data



from dissociation pressure measurements; Mills [1974MIL] evaluated these results. Sharma and Chang [1986SHA/CHA] regard this compound as a metastable phase and not part of the equilibrium S-Sn phase diagram. This conclusion was corroborated by the careful preparative and analytical work of [2003CRU/MOR] and is adopted here. “Sn<sub>3</sub>S<sub>4</sub>” has probably been confused with a mixture of SnS + Sn<sub>2</sub>S<sub>3</sub>.

#### IX.1.1.2.6 Sn<sub>4</sub>S<sub>5</sub>(cr)

This compound was postulated [1937GER/KRU] as an intermediate product in the decomposition of SnS<sub>2</sub>. It is not considered part of the equilibrium S-Sn phase diagram ([1961ALB/SCH], [1962MOH], [1969MOH]). This conclusion was corroborated by [2003CRU/MOR] and is adopted here. “Sn<sub>4</sub>S<sub>5</sub>” has probably been confused with a mixture of 2 SnS + Sn<sub>2</sub>S<sub>3</sub>.

#### IX.1.1.2.7 Ternary tin sulfides

##### *Cu<sub>8</sub>SnS<sub>6</sub>(cr)*

The heat capacity was measured [1989ALI/DZH] at 55 to 100 K by adiabatic calorimetry (uncertainty ± 1%) and at 77 to 420 K by light pulse heating (uncertainty ± 8%). The data were not tabulated, and appear only in a graph. The  $C_{p,m}^{\circ}$  vs.  $T$  curve shows a smooth rise from 55 to 300 K, after which there is a local narrow peak (from 365 to 1250 J·K<sup>-1</sup>·mol<sup>-1</sup>). The peak is clearly defined at 328 K, after which the heat capacity returns to its previous value. This thermal event was called a first-order transition [1989ALI/DZH], *i.e.*, a solid-solid transformation. The enthalpy change in the phase transition was reported as (5.1 ± 0.3) kJ·mol<sup>-1</sup>.

There is no report of the enthalpy of formation of this compound.

The selected heat capacity at 298.15 K is (365 ± 29) J·K<sup>-1</sup>·mol<sup>-1</sup>.

##### *Cu<sub>4</sub>SnS<sub>4</sub>(cr)*

The heat capacity was measured at 80 to 400 K by adiabatic calorimetry and DSC [1983ALI/ARA]. The data were not tabulated and appear only in a graph. The heat capacity varied approximately linearly over the experimental temperature range, from 180 to 257 J·K<sup>-1</sup>·mol<sup>-1</sup>. Its value at 298 K was read from the  $C_{p,m}^{\circ}$  vs.  $T$  plot. There is a local maximum [1974KHA/RIV], [1983ALI/ARA] at 232 K which may be attributed to a solid-solid transition. The enthalpy of this phase transition is ≈ 2.5 kJ·mol<sup>-1</sup> [1983ALI/ARA]. The compound decomposes at 1083 K before melting [1974KHA/RIV].

Cell potential measurements were performed at 300 to 420 K [1987MUS/ABB]. Both  $S_m^{\circ}$  (Cu<sub>4</sub>SnS<sub>4</sub>, cr,  $T$ ) and  $\Delta_f H_m^{\circ}$  (Cu<sub>4</sub>SnS<sub>4</sub>, cr,  $T$ ) were derived therefrom.

The selected heat capacity at 298 K is:

$$C_{p,m}^{\circ}(\text{Cu}_4\text{SnS}_4, \text{cr}, 298.15 \text{ K}) = (230.0 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

(present evaluation).

The selected formation properties are

$$S_{\text{m}}^{\circ}(\text{Cu}_4\text{SnS}_4, \text{cr}, 298.15 \text{ K}) = (414 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cu}_4\text{SnS}_4, \text{cr}, 298.15 \text{ K}) = -(220.8 \pm 9.4) \text{ kJ}\cdot\text{mol}^{-1},$$

yielding:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Cu}_4\text{SnS}_4, \text{cr}, 298.15 \text{ K}) = -(251.2 \pm 11.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### *Cu<sub>2</sub>SnS<sub>3</sub>(cr)*

This compound melts congruently at 1123 K [1974KHA/RIV]. There is no report of its heat capacity. Selected standard formation properties were derived from cell-potential measurements at 300 to 420 K [1987MUS/ABB]:

$$S_{\text{m}}^{\circ}(\text{Cu}_2\text{SnS}_3, \text{cr}, 298.15 \text{ K}) = (279 \pm 1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cu}_2\text{SnS}_3, \text{cr}, 298.15 \text{ K}) = -(150.0 \pm 5.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Cu}_2\text{SnS}_3, \text{cr}, 298.15 \text{ K}) = -(169.5 \pm 5.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### *Cu<sub>2</sub>Sn<sub>4</sub>S<sub>9</sub>(cr)*

This compound decomposes at 938 K before melting [1974KHA/RIV]. There is no report of its heat capacity. Selected standard formation properties were derived from cell-potential measurements at 300 to 420 K [1987MUS/ABB]:

$$S_{\text{m}}^{\circ}(\text{Cu}_2\text{Sn}_4\text{S}_9, \text{cr}, 298.15 \text{ K}) = (640 \pm 18) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cu}_2\text{Sn}_4\text{S}_9, \text{cr}, 298.15 \text{ K}) = -(141.6 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Cu}_2\text{Sn}_4\text{S}_9, \text{cr}, 298.15 \text{ K}) = -(165.6 \pm 8.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### *Cu<sub>4</sub>Sn<sub>3</sub>S<sub>8</sub>(cr)*

According to [1974KHA/RIV], this compound is stable only at high temperature.

### IX.1.1.3 Solubility of tin sulfides

Despite the practical importance surprisingly few experimental investigations on the solubility of tin sulfides in aqueous solutions are known. In the tin ore deposits formed under hydrothermal conditions besides cassiterite (SnO<sub>2</sub>), the quite rare sulfidic

minerals Herzenbergite (SnS), Berndtite ( $\beta$ -SnS<sub>2</sub>) and Ottemannite (Sn<sub>2</sub>S<sub>3</sub>) are found.  $\beta$ -SnS<sub>2</sub> occurs in several polytypic modifications [1974MIT/FUJ]. About the behaviour of Sn<sub>2</sub>S<sub>3</sub> in contact with aqueous solutions only some general remarks from Moh and Berndt [1964MOH/BER] are available.

Experimental work with sparingly soluble tin sulfides meets a number of difficulties. This concerns hydrolysis of aqua complexes of Sn<sup>2+</sup> and Sn<sup>4+</sup> taking place already in acid solutions, oxidation of tin(II) in solution by dissolved oxygen (Reaction (IX.6)) or sulfur (Reaction (IX.7)). Sulfur is formed easily by oxidation of H<sub>2</sub>S by oxygen. Oxidation with sulfur (Reaction (IX.7)) is reversible, especially at higher pH, prolonged equilibration of Sn<sup>4+</sup>-containing solutions generates sulfur and through Reaction (IX.8) thiocomplexes. Evaluation of the experimental results is complicated by the formation of numerous hydrolytic and complex species of tin(II) and tin(IV).



#### IX.1.1.3.1 Solubility of SnS(cr)

Solubility products of SnS mostly cited in literature are those of Latimer ( $1 \times 10^{-26}$ ) [1952LAT] and of Kapustinskii ( $1 \times 10^{-27}$ ) [1940KAP], [1938KAP/MAK] based on thermodynamic estimations and calculations. A dependence of the SnS solubility on pH was calculated by Kapustinskii [1940KAP], which yielded values of  $9.6 \times 10^{-7}$  M at pH = 3 and  $9.7 \times 10^{-9}$  M at pH = 5.

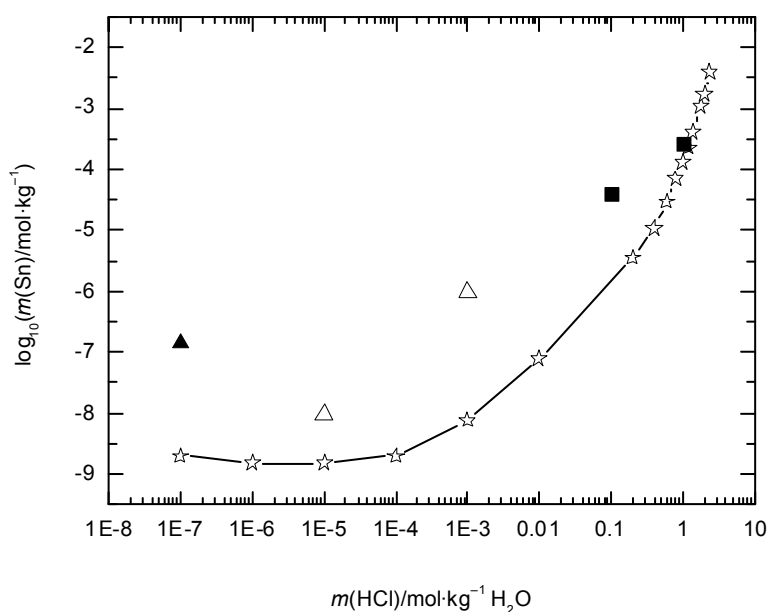
An experimental determination of the solubility of SnS in 0.1 and 1.0 M HCl was performed by Geyer and Mücke [1964GEY/MUC]. Care was taken to avoid oxidation during preparation of the sulfide and all analytical operations (see Appendix). Results are listed in Table IX-14.

Table IX-14: Solubility of SnS in aqueous HCl at 293 K.

$c_{\text{HCl}}/\text{M}$	$s_{\text{SnS}}/\text{M}$
0.1	$3.9 \times 10^{-5}$
0.1	$4.0 \times 10^{-5}$
0.1	$4.0 \times 10^{-5}$
1.0	$2.7 \times 10^{-4}$
1.0	$2.6 \times 10^{-4}$
1.0	$2.4 \times 10^{-4}$

These values can be compared with calculated solubilities using the selected and auxiliary standard formation data for solid phase, sulfur-containing species and chlorido complexes of tin given in this volume Figure IX-4. The agreement with the experimental data of Geyer and Mücke seems to be satisfactory and lends support to the database established in this review. At concentrations of  $H^+$  below  $0.01 \text{ mol}\cdot\text{kg}^{-1}$  tin speciation is dominated by hydroxido complexes and above this  $H^+$  concentration chlorido complex formation starts to dominate. The calculations of Kapustinskii do not include hydrolysis. The virtual straight line, which can be drawn through the experimental data of [1964GEY/MUC] and calculated points of [1940KAP] has to be considered as accidental. Weigel [1907WEI] determined the dissolved ion concentrations by measurement of the electrical conductivity assuming  $\text{Sn}^{2+}$  and  $\text{S}^{2-}$  as governing ions, which is not true (see Appendix A).

Figure IX-4: Solubility of SnS in aqueous HCl (■: experimental data at 293 K [1964GEY/MUC];  $\Delta$ : calculated data [1940KAP];  $\blacktriangle$ : experimental data at 291 K [1907WEI];  $\star$ : calculated by this review).



### IX.1.1.3.2 Solubility of $\text{SnS}_2(\text{cr})$

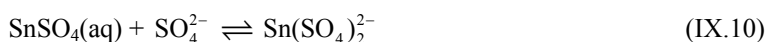
Weigel determined the solubility of  $\text{SnS}_2$  in water to be  $s = 1.13 \times 10^{-6} \text{ M}$  at 271 K using a commercial sample of "Musivgold" [1906WEI], [1907WEI]. Solubility data published by Sorum and Wolf [1950SOR/WOL] are obviously too high ( $s = 10^{-2} \text{ M}$  at

299 K,  $s = 0.7$  M at 333 K). Babko and Lisetskaya [1956BAB/LIS] report data on solubility of very finely dispersed or colloidal  $\text{SnS}_2$  in dependence of pH (pH = 8 to 12,  $10^{-5}$  to  $10^{-2}$  M) at 273 K. A series of solubility determinations in relatively concentrated solutions of HCl and  $\text{CaCl}_2$  has been performed by Topgyna and Kochetkova [1983TOP/KOC], [1984KOC/TOP] at 298 K. On the basis of thermodynamic modelling from the collected results, the Gibbs energy of formation of  $\text{SnS}_2$  was estimated to be  $-180.75$   $\text{kJ}\cdot\text{mol}^{-1}$  for a good crystallised product and  $-172.80$   $\text{kJ}\cdot\text{mol}^{-1}$  for a nearly amorphous product [1984KOC/TOP]. These values of  $\Delta_f G_m^\circ(\text{SnS}_2, s, 298.15 \text{ K})$  are 30 – 40  $\text{kJ}\cdot\text{mol}^{-1}$  more negative than the value of  $-143$   $\text{kJ}\cdot\text{mol}^{-1}$  obtained from the data recommended in this review. The model and experimental data of [1984KOC/TOP] are obviously not suitable for the derivation of standard thermodynamic quantities (see Appendix A).

## IX.1.2 Tin sulfates

### IX.1.2.1 Aqueous sulfato complexes of tin(II)

Only two papers report equilibrium data for the  $\text{SnSO}_4(\text{aq})$  complex [1975WAD/ITO] and [1981PET/MIL]. Since in the latter work the authors applied very high  $[\text{SO}_4^{2-}]/[\text{Sn}^{2+}]$  ratios (up to  $1.5 \times 10^6$ ), they also detected the formation of a *bis*-complex (Eq.(IX.10)).



The recalculated constants for zero ionic strength – based on the published data – are rather different (see Table IX-15). In the case of [1981PET/MIL] the calculation is based on a few points determined with increasing concentration of the self medium ( $\text{Na}_2\text{SO}_4$ ). On the other hand, [1975WAD/ITO] performed potentiometric titrations at several ionic strengths, therefore our SIT treatment (Figure IX-5) was based only on their values. Nevertheless, the  $\log_{10} \beta_1$  value derived from the data of [1981PET/MIL] at constant ionic strength ( $I = 1.5$  M)  $\text{Na}(\text{NO}_3, \text{SO}_4)$  agrees relatively well with the value extrapolated by using the data reported in [1975WAD/ITO] (see filled square in Figure IX-5). It should be mentioned, that in [1975WAD/ITO] the authors evaluated their data by assuming the formation of  $\text{Sn}(\text{HSO}_4)^+$  as well as the species  $\text{SnSO}_4(\text{aq})$ . However, the SIT treatment of the data reported for the reaction  $\text{Sn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{SnSO}_4(\text{aq})$  resulted in an unreliably high  $\Delta\varepsilon$  value ( $\Delta\varepsilon = 0.85$   $\text{kg}\cdot\text{mol}^{-1}$ ), therefore in our re-evaluation the formation of the latter species was neglected.

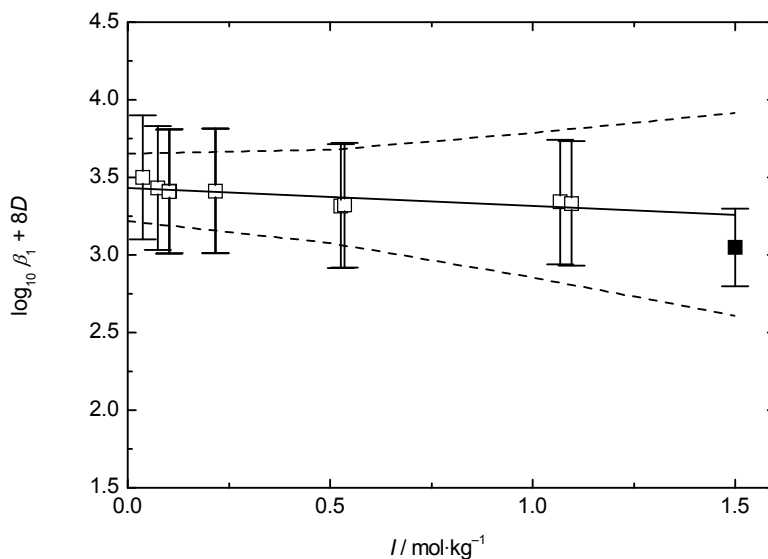
Table IX-15: Experimental equilibrium constants for sulfato complexes of tin(II).

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} K$ reported	$\log_{10} K$ recalculated <sup>(a)</sup>	$\log_{10} K$ accepted <sup>(b)</sup>	Reference
<b><math>\text{Sn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{SnSO}_4(\text{aq})</math></b>						
vol	1.5 M $\text{NaNO}_3$	20	$1.29 \pm 0.10$	$1.29 \pm 0.25$	$1.27 \pm 0.20$	[1981PET/MIL]
	$\rightarrow 0$ ( $\text{Na}_2\text{SO}_4$ )	20		$2.2 \pm 0.5$	$1.7 \pm 0.5$	
Ise-Sn	1 M (H,Na) $\text{ClO}_4$	25	1.70			[1975WAD/ITO]
	0.52 M (H,Na) $\text{ClO}_4$	25	1.91			
	0.21 M (H,Na) $\text{ClO}_4$	25	2.30			
	0.1 M (H,Na) $\text{ClO}_4$	25	2.53			
	0.075 M (H,Na) $\text{ClO}_4$	25	2.64			
	0.037 M (H,Na) $\text{ClO}_4$	25	2.89			
	$\rightarrow 0$ ((Na,H) $\text{ClO}_4$ )	25	$3.37 \pm 0.12$	$3.43 \pm 0.17$	$3.43 \pm 0.25$	
<b><math>\text{Sn}^{2+} + 2 \text{SO}_4^{2-} \rightleftharpoons \text{Sn}(\text{SO}_4)_2^{2-}</math></b>						
vol	1.5 M $\text{NaNO}_3$	20	$1.65 \pm 0.10$	$1.73 \pm 0.30$		[1981PET/MIL]
	$\rightarrow 0$ ( $\text{Na}_2\text{SO}_4$ )	20		$3.3 \pm 0.5$		

(a) Re-evaluated value (see Appendix A).

(b) Accepted values corrected to molal scale.

Figure IX-5: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{SnSO}_4(\text{aq})$  in  $\text{NaClO}_4$  media at  $25^\circ\text{C}$  ( $\square$ : experimental data from [1975WAD/ITO],  $\blacksquare$ : experimental data from [1981PET/MIL] for  $\text{Na}_2\text{SO}_4$  background at  $20^\circ\text{C}$ , not included in the SIT analysis).



The SIT analysis of the experimental constants reported in [1975WAD/ITO] for Reaction (IX.9) in perchlorate media at 25 °C (Figure IX-5), resulted in the following values

$$\log_{10} \beta_1^{\circ} ((\text{IX.9}), 298.15 \text{ K}) = (3.43 \pm 0.25)$$

and  $\Delta \varepsilon(\text{IX.9}) = (0.11 \pm 0.33) \text{ kg}\cdot\text{mol}^{-1}$ . From  $\Delta \varepsilon(\text{IX.9})$ , the ion interaction coefficient  $\varepsilon(\text{SnSO}_4(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.19 \pm 0.35) \text{ kg}\cdot\text{mol}^{-1}$  can be calculated, which is a relatively high value for a neutral species, however considering the uncertainty range, it is acceptable. The above  $\log_{10} \beta_1^{\circ}$  value is slightly higher than expected based on the recently reviewed  $\text{Pb}^{2+}\text{-SO}_4^{2-}$  system ( $\log_{10} \beta_1^{\circ} = (2.72 \pm 0.05)$ , [2009POW/BRO]).

The selected thermodynamic formation constant, listed above, corresponds to

$$\Delta_r G_m^{\circ} ((\text{IX.9}), 298.15 \text{ K}) = -(19.6 \pm 1.4) \text{ kJ mol}^{-1},$$

and hence

$$\Delta_r G_m^{\circ} (\text{SnSO}_4, \text{aq}, 298.15 \text{ K}) = -(791.0 \pm 1.5) \text{ kJ mol}^{-1}.$$

Wada and Ito also studied the temperature dependence of complex formation processes at  $I = 0.5 \text{ M}$  and at four different temperatures between 15 and 45 °C [1975WAD/ITO]. The authors reported  $\Delta_r H_m^{\circ} ((\text{IX.9}), I = 0.5 \text{ M NaClO}_4) = 16.9 \text{ kJ}\cdot\text{mol}^{-1}$ , which can be used as tentative value for  $\Delta_r H_m^{\circ} (\text{IX.9})$ .

### IX.1.2.2 Aqueous sulfato complexes of tin(IV)

The complex formation between tin(IV) and sulfate ion has been studied by Brubaker [1954BRU], [1955BRU], [1957BRU]. He explained the solubility of  $\text{SnO}_2$  in 0.2 to 1.0 M  $\text{H}_2\text{SO}_4$  solution by Reaction (IX.11),



and reported the value  $\log_{10} K^{\circ} ((\text{IX.11}), 303.15 \text{ K}) = -1.30$  and  $\log_{10} K^{\circ} ((\text{IX.11}), 291.15 \text{ K}) = -1.55$  [1955BRU]. In 1.0 to 4.0 M sulfuric acid solution Brubaker reported the formation of *bis*-sulfato complex ( $\text{SnSO}_4^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{H}_2\text{Sn}(\text{SO}_4)_2(\text{aq})$ ,  $K \approx 100$ ) [1957BRU]. Although the existence of tin(IV)-sulfato complexes is indisputable, due to the reasons mentioned in Appendix A, the above equilibrium constants cannot be used to derive selected values.

### IX.1.2.3 Solid tin sulfates

Anhydrous  $\text{SnSO}_4$  can be prepared from aqueous solutions containing an excess of sulfuric acid [1926CAR], [1960DON/MOS]. In oxygen-free atmosphere it is thermally stable until 360 – 370 °C [1960DON/MOS]. Crystal structure analysis reveals trigonal pyramidal coordination of tin by oxygen atoms of three different sulfate groups [1972DON/PUX]. No evidence for a hydrated form of neutral tin(II) sulfate exists. Due

to hydrolysis solubility measurements are rare and only tentative. According to [1960DON/MOS] quite concentrated, transparent aqueous solutions are obtained by adding water to the sulfate. Mass concentration varies from 352 g·dm<sup>-3</sup> SnSO<sub>4</sub> at 20 °C to 220 g·dm<sup>-3</sup> at 100 °C [1960DON/MOS]. In 0.5 M sulfuric acid the corresponding amounts of dissolved SnSO<sub>4</sub> are lower (23.2 g·dm<sup>-3</sup> at 20 °C, 13.2 g·dm<sup>-3</sup> at 100 °C). The stability field of SnSO<sub>4</sub> and its hydrolysis products in the system SnO-SO<sub>3</sub>-H<sub>2</sub>O have been determined by Denham and King at 25 °C and 50 °C [1935DEN/KIN]. Solubility of SnSO<sub>4</sub> drops sharply with increasing concentration of H<sub>2</sub>SO<sub>4</sub>, however, no solubility constant can be derived from the data.

### IX.1.2.4 Basic tin(II) sulfate

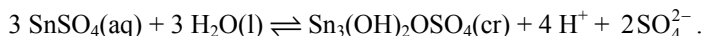
#### IX.1.2.4.1 Composition of basic tin(II) sulfate

From dilute aqueous solutions of tin(II) sulfate with a pH not higher than 2.4 a basic compound Sn<sub>3</sub>(OH)<sub>2</sub>OSO<sub>4</sub>, tritin(II) dihydroxide oxide sulfate, crystallises [1967DAV/DON], the crystal structure of which was determined [1975DAV/DON], [1975GRI]. Several hydrated forms have been discussed on the basis of chemical analyses [1882DIT2], [1926CAR], [1935DEN/KIN]. According to the study of [1935DEN/KIN] at higher sulfate concentrations the compound SnSO<sub>4</sub>·SnO represents an equilibrium phase in aqueous solutions at 25 °C and 50 °C. Lundgren *et al.* performed a crystal structure analysis of SnSO<sub>4</sub>·SnO [1982LUN/WER].

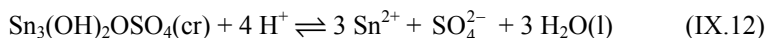
Basic tin(II) sulfate is a rare corrosion product found on the surfaces of tin and tin alloys. Tin(II) oxide sulfate, Sn<sub>3</sub>O<sub>2</sub>SO<sub>4</sub>, was identified on concretions of corroding bronze objects recovered from seawater [1982MAC].

#### IX.1.2.4.2 Solubility of Sn<sub>3</sub>(OH)<sub>2</sub>OSO<sub>4</sub>

Edwards *et al.* [1996EDW/GIL] precipitated Sn<sub>3</sub>(OH)<sub>2</sub>OSO<sub>4</sub>(cr) by hydrolysis of tin(II) sulfate according to the following reaction



The dissolution reaction



was studied by measuring the activities of hydrogen ion, tin(II) ion and sulfate ion with glass, tin amalgam and sulfate ion selective electrodes, respectively. With  $\log_{10} K_s^\circ$  (IX.12) =  $-(5.01 \pm 0.37)$ , see Appendix A, thermodynamic auxiliary data for SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>O(l) taken from Table IV-1 and with  $\Delta_f G_m^\circ$  (Sn<sup>2+</sup>, 298.15 K) selected by this review

$$\Delta_f G_m^\circ (\text{Sn}_3(\text{OH})_2\text{OSO}_4, \text{cr}, 298.15 \text{ K}) = -(1566.2 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$$

has been obtained.



Unfortunately, the authors do not describe all details of activity calibrations in  $\text{NaClO}_4$  solution and do not explain how they corrected the observed “interference of the potential of the sulfate electrode by  $\text{Sn}^{2+}$ ”. Therefore, this value of  $\Delta_f G_m^\circ (\text{Sn}_3(\text{OH})_2\text{OSO}_4, \text{cr}, 298.15 \text{ K})$  can be affected by systematic errors and cannot be selected.



# Chapter X

## Group 15 compounds and complexes

### X.1 Nitrogen compounds and complexes

#### X.1.1 Aqueous tin(II) nitrate complexes

Nitrate ion forms weak complexes (ion pairs) with divalent metal ions such as tin(II). Consequently, high excesses of nitrate over tin(II) should be used, *i.e.* a large part of the medium ions are replaced by the complex-forming electrolyte, to assess the stability of the complexes formed. Under such conditions the differentiation between complex formation and medium effect is not obvious. Solution equilibrium data on the nitrate complexes of tin(II) can be found only in [1980AND/SAM]. Based on the experimental data obtained at six different ionic strengths, the authors suggested the following equilibrium processes



Since increasing excess of nitrate over tin(II) can be used with increasing ionic strength, at  $I = 1$  M Na(ClO<sub>4</sub>,NO<sub>3</sub>) only a single species ( $q = 1$ ) was detected, while the formation of four complexes ( $q = 1$  to 4) was reported at  $I \geq 4$  M Na(ClO<sub>4</sub>, NO<sub>3</sub>). Spectroscopic evidence for the existence of tin(II) nitrate complexes is not available. Moreover, nitrate complexes of tin(II) were not detected by Pettine *et al.* [1981PET/MIL]. On the other hand, a concordant data set is in favour for the formation of nitrate complexes of the related lead(II) [1999LOT/OCH]. The primary data are reported in [1980AND/SAM], unfortunately only for  $I = 3$  M, using the data points corresponding to  $[\text{NO}_3^-]_{\text{tot}} \leq 0.6$  M (maximum 20% replacement of the background electrolyte), were re-evaluated for the purpose of this review (see discussion on [1980AND/SAM]). At  $I = 3$  M the formation of three complexes ( $\text{SnNO}_3^+$ ,  $\text{Sn}(\text{NO}_3)_2(\text{aq})$ ,  $\text{Sn}(\text{NO}_3)_3^-$ ) was reported in [1980AND/SAM]. Using the above mentioned limited data set, the experimental data can be well reproduced considering the formation of  $\text{SnNO}_3^+$  and  $\text{Sn}(\text{NO}_3)_2(\text{aq})$  (see Appendix A). Therefore, the formation of the *tris*-nitrate complex, reported in [1980AND/SAM] is ambiguous, since the differentiation between complex formation and medium effect is almost impossible at higher nitrate concentrations. For this reason, in this review only the formation of

$\text{SnNO}_3^+$  and  $\text{Sn}(\text{NO}_3)_2(\text{aq})$  is considered (see also discussion on [1980AND/SAM]). The experimental formation constants for the Reactions (X.1) are collected in Table X-1.

The accepted formation constants were extrapolated to zero ionic strength using the SIT. The weighted linear regression of the five data points for  $\text{SnNO}_3^+$  (Figure X-1), resulted in the selected constant

$$\log_{10} \beta_1^0 ((\text{X.1}), q = 1, 298.15 \text{ K}) = (1.27 \pm 0.31).$$

The determined value of  $\Delta \varepsilon(\text{X.1}), q = 1$  is  $(0.02 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$ , which corresponds to the ion interaction coefficient  $\varepsilon(\text{SnNO}_3^+, \text{ClO}_4^-) = (0.17 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ .

Table X-1: Experimental formation constants of the species  $\text{Sn}(\text{NO}_3)_q^{2-q}$ .

Method	Ionic media	$t/^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			Reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{NO}_3^- \rightleftharpoons \text{SnNO}_3^+$						
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	$0.44 \pm 0.02$		$0.42 \pm 0.40$	[1980AND/SAM]
	2.0 M NaClO <sub>4</sub>	25	$0.41 \pm 0.02$		$0.37 \pm 0.40$	
	3.0 M NaClO <sub>4</sub>	25	$0.14 \pm 0.02$	$0.23 \pm 0.02$	$0.16 \pm 0.30$	
	4.0 M NaClO <sub>4</sub>	25	$0.15 \pm 0.03$		$0.06 \pm 0.40$	
	6.0 M NaClO <sub>4</sub>	25	$0.18 \pm 0.03$		$0.01 \pm 0.40$	
	8.0 M NaClO <sub>4</sub>	25	$0.43 \pm 0.04$			
$\text{Sn}^{2+} + 2 \text{NO}_3^- \rightleftharpoons \text{Sn}(\text{NO}_3)_2(\text{aq})$						
Ise-Sn	2.0 M NaClO <sub>4</sub>	25	$0.45 \pm 0.05$			[1980AND/SAM]
	3.0 M NaClO <sub>4</sub>	25	$0.05 \pm 0.02$	$0.04 \pm 0.02$	$-0.09 \pm 0.30$	
	4.0 M NaClO <sub>4</sub>	25	$-0.06 \pm 0.06$		$-0.24 \pm 0.40$	
	6.0 M NaClO <sub>4</sub>	25	$0.00 \pm 0.08$		$-0.34 \pm 0.40$	
	8.0 M NaClO <sub>4</sub>	25	$0.57 \pm 0.05$			
$\text{Sn}^{2+} + 3 \text{NO}_3^- \rightleftharpoons \text{Sn}(\text{NO}_3)_3^-$						
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	$-0.35 \pm 0.10$			[1980AND/SAM]
	4.0 M NaClO <sub>4</sub>	25	$-0.58 \pm 0.11$			
	6.0 M NaClO <sub>4</sub>	25	$-0.85 \pm 0.12$			
	8.0 M NaClO <sub>4</sub>	25	$0.46 \pm 0.11$			
$\text{Sn}^{2+} + 4 \text{NO}_3^- \rightleftharpoons \text{Sn}(\text{NO}_3)_4^{2-}$						
Ise-Sn	4.0 M NaClO <sub>4</sub>	25	$-0.98 \pm 0.20$			[1980AND/SAM]
	6.0 M NaClO <sub>4</sub>	25	$-1.20 \pm 0.20$			
	8.0 M NaClO <sub>4</sub>	25	$-0.01 \pm 0.15$			

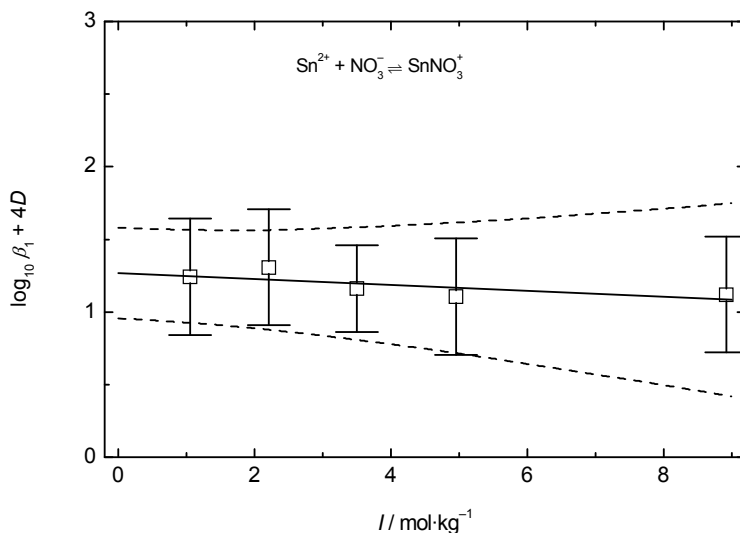
(a) Re-evaluated values, see Appendix A.

(b) Accepted values corrected to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

Figure X-2 shows the result of the SIT extrapolation to  $I = 0$  of the values of  $\log_{10} \beta_2^0$  listed in Table X-1. The selected value from the weighted linear regression is

$$\log_{10} \beta_2^0 ((X.1), q = 2, 298.15 \text{ K}) = (1.39 \pm 0.53).$$

Figure X-1: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{NO}_3^- \rightleftharpoons \text{SnNO}_3^+$  in  $\text{NaClO}_4$  media.



The corresponding ion interaction coefficient is  $\Delta\alpha((X.1), q = 2) = (0.01 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ . Using this value,  $\alpha(\text{Sn}(\text{NO}_3)_2(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.130 \pm 0.011) \text{ kg}\cdot\text{mol}^{-1}$  can be derived.

The selected thermodynamic formation constants correspond to

$$\Delta_r G_m^\circ ((X.1), q = 1, 298.15 \text{ K}) = -(7.25 \pm 1.77) \text{ kJ}\cdot\text{mol}^{-1},$$

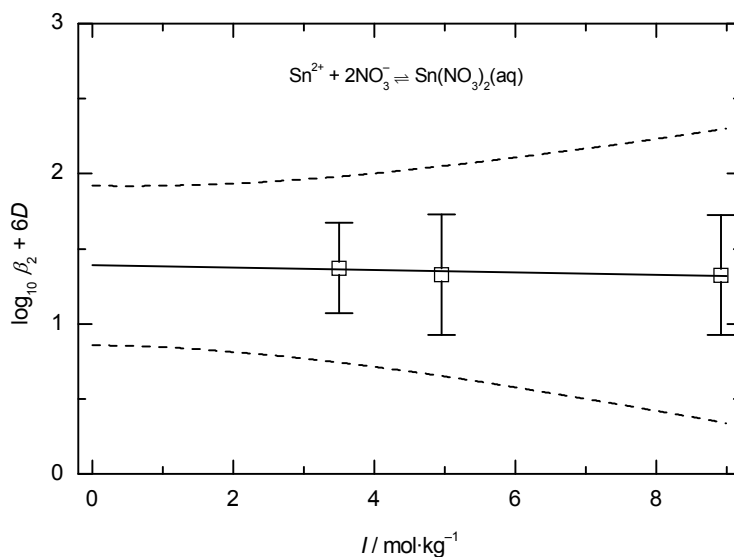
$$\Delta_r G_m^\circ ((X.1), q = 2, 298.15 \text{ K}) = -(7.9 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1},$$

and hence

$$\Delta_f G_m^\circ (\text{SnNO}_3^+, 298.15 \text{ K}) = -(145.4 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f G_m^\circ (\text{Sn}(\text{NO}_3)_2(\text{aq}), 298.15 \text{ K}) = -(256.9 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

Figure X-2: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Sn}(\text{NO}_3)_2(\text{aq})$  in  $\text{NaClO}_4$  media.



## X.2 Phosphorus compounds and complexes

### X.2.1 Solid tin phosphide

Tin forms a ternary compound with silver, phosphorus and germanium with the formula  $(\text{Ag}_6\text{Sn}_4\text{P}_{12})\text{Ge}_6$ . The crystal structure is cubic in the space group  $I\bar{4}3m$  (No. 217) with lattice parameters  $a = 10.430(3)$  Å,  $Z = 2$  [1976SCH/HAU], [1979HON/SCH], [1980HON/SCH].

Gmelin *et al.* [1989GME/HON] determined the standard enthalpy of formation using the heats of reaction data on  $(\text{Ag}_6\text{Sn}_4\text{P}_{12})\text{Ge}_6(\text{cr}) \rightleftharpoons 6 \text{Ag}(\text{cr}) + 6 \text{Ge}(\text{cr}) + 4 \text{Sn}(\text{l}) + 3 \text{P}_4(\text{g})$ . They calculated the second and third law values using the elemental data from Kubaschewski and Alcock [1979KUB/ALC] and obtained the following value:

$$\Delta_f H_m^\circ (\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6, \text{cr}, 298.15 \text{ K}) = -(147.0 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

Gmelin *et al.* [1989GME/HON] used an automated adiabatic calorimeter to determine the specific heat in the temperature range from 2 to 100 K. Above 100 K, they used a Perkin-Elmer DSC-2 scanning calorimeter; the errors in temperature were less than 0.15 degree and in the calorimetric data, the errors were less than 1.5%. Their data from 230 to 320 K result in  $C_{p,m}^\circ (\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6, \text{cr}, T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (556.2 \pm 8.7) + (0.3406 \pm 0.0208) T/\text{K} - (2.572 \pm 0.217) \times 10^6 (T/\text{K})^{-2}$ , leading to:

$$C_{p,m}^{\circ}(\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6, \text{cr}, 298.15 \text{ K}) = (628.82 \pm 9.40) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Enthalpy increment, entropy and Gibbs energy increment depending on temperature have been obtained by numerical integration of the smoothed heat capacity values listed in Table X-2, resulting in:

$$S_m^{\circ}(\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6, \text{cr}, 298.15 \text{ K}) = (903.13 \pm 13.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

These values of  $\Delta_f H_m^{\circ}$ ,  $C_{p,m}^{\circ}$ , and  $S_m^{\circ}$  of  $\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6(\text{cr})$  at 298.15 K are selected by this review, and yield:

$$\Delta_f G_m^{\circ}(\text{Ag}_6\text{Sn}_4\text{P}_{12}\text{Ge}_6, \text{cr}, 298.15 \text{ K}) = - (78.48 \pm 4.00) \text{ kJ}\cdot\text{mol}^{-1}.$$

Table X-2: Smoothed calorimetric values for  $[\text{Ag}_6\text{Sn}_4\text{P}_{12}]\text{Ge}_6$  [1989GME/HON].

$T / \text{K}$	$C_{p,m}^{\circ} / \text{J}\cdot\text{mol}^{-1} \text{ K}^{-1}$	$H(T) - H(0\text{K}) / \text{kJ}\cdot\text{mol}^{-1}$	$S_m^{\circ} / \text{J}\cdot\text{mol}^{-1} \text{ K}^{-1}$	$-(G(T) - G(0\text{K})) / \text{kJ}\cdot\text{mol}^{-1}$
3.5	-	0.2204	0.1038	0.1429
4	0.27898	0.33845	0.13521	0.20239
4.5	0.39749	0.50566	0.17446	0.27944
5	0.56773	0.74448	0.22464	0.37871
6	1.1179	1.5608	0.37198	0.67101
7	2.0389	3.1036	0.60800	1.1523
8	3.3981	5.7811	0.96351	1.9269
9	5.2013	10.044	1.4636	3.1279
10	7.4257	16.323	2.1231	4.9077
12	13.072	36.563	3.9526	10.868
14	20.198	69.600	6.4849	21.188
16	28.645	118.23	9.7197	37.277
18	38.238	184.94	13.637	60.523
20	48.784	271.82	18.204	92.259
25	77.908	587.36	32.165	216.77
30	107.90	1052.3	49.039	418.78
35	134.34	1660.5	67.734	710.21
40	167.80	2427.6	88.178	1099.4
45	193.80	3332.9	109.47	1593.3
50	216.89	4360.8	131.11	2194.8
55	237.54	5497.8	152.77	2904.5
60	256.23	6733.0	174.25	3722.2
65	273.41	8057.6	195.44	4646.6
70	289.55	9465.3	216.30	5676.1
75	305.11	10952	236.81	6809.0
80	320.57	12516	257.00	8043.7

(Continued on next page)

Table X-2 (continued)

<i>T/K</i>	$C_{p,m}^{\circ} / \text{J}\cdot\text{mol}^{-1} \text{K}^{-1}$	$H(T) - H(0\text{K}) /$ $\text{kJ}\cdot\text{mol}^{-1}$	$S_m^{\circ} / \text{J}\cdot\text{mol}^{-1} \text{K}^{-1}$	$-(G(T) - G(0\text{K})) /$ $\text{kJ}\cdot\text{mol}^{-1}$
85	336.40	14158	276.90	9378.6
90	353.04	15881	296.60	10812
95	370.99	17691	316.16	12344
100	389.44	19607	335.81	13974
110	413.13	23621	374.06	17525
120	435.06	27864	410.96	21451
130	455.32	32317	446.59	25740
140	474.01	36965	481.03	30379
150	491.20	41792	514.33	35357
160	506.98	46784	546.54	40662
170	521.45	51928	577.72	46284
180	534.69	57209	607.90	52213
190	546.79	62618	637.14	58439
200	557.83	68142	665.47	64953
220	577.12	79496	719.57	78809
240	593.25	91205	770.50	93714
260	606.92	103210	818.54	109609
280	618.84	115470	863.96	126439
298.15	628.73	126792	903.13	142478
300	629.71	127957	907.03	144152
320	640.24	140656	948.01	162706

## X.2.2 Aqueous tin phosphato complexes

### X.2.2.1 Aqueous tin(II) phosphato complexes

Only two reports are available on the formation of phosphato complexes of tin(II) [1968CIL], [2000CIA/IUL2]. Cilley performed a solubility study at constant pH [1968CIL], which gives no information on the protonation state of the coordinated ligand(s). Therefore, the complex formation constants reported in [1968CIL] were not considered in this review. The potentiometric titrations reported in [2000CIA/IUL2] using both tin amalgam and glass electrodes revealed the formation of seven complex species:  $\text{SnH}_2\text{PO}_4^+$ ,  $\text{Sn}(\text{H}_2\text{PO}_4)_2(\text{aq})$ ,  $\text{Sn}(\text{H}_2\text{PO}_4)(\text{HPO}_4)^-$ ,  $\text{SnHPO}_4(\text{aq})$ ,  $\text{Sn}(\text{HPO}_4)_2^{2-}$ ,  $\text{Sn}(\text{HPO}_4)_3^{4-}$  and  $\text{SnPO}_4^-$ . The formation of similar complexes was suggested for several other divalent metal ions [1970CHI], [2001CIA]. Among these complexes only the species  $\text{SnHPO}_4(\text{aq})$  and  $\text{SnPO}_4^-$  are important under nearly environmental conditions (Figure X-3). The constants obtained in [2000CIA/IUL2] at  $I = 3 \text{ M}$  ( $\text{NaClO}_4$ ) were extrapolated to  $I = 0$ , using several estimated ion interaction coefficients



(see Table X-3 and Appendix A). One has to mention, that the complexes such as  $\text{SnHPO}_4(\text{aq})$  and  $\text{Sn}(\text{OH})_2\text{PO}_4(\text{aq})$ , or  $\text{SnPO}_4^-$ ,  $\text{Sn}(\text{OH})\text{HPO}_4^-$  and  $\text{Sn}(\text{OH})_2(\text{H}_2\text{PO}_4)^-$  cannot be distinguished by potentiometric measurements. Therefore, the validity of the ion interaction coefficients estimated using Eqs.(B.22) and (B.23) (Appendix B) is uncertain. Consequently, the thermodynamic formation constants reported in [2000CIA/IUL2] are not selected in this review, but they can be used until more data will be published on this system.

Figure X-3: Speciation diagram for the tin(II)-orthophosphate system at  $I = 3 \text{ M}$  ( $\text{NaClO}_4$ ) with total concentrations  $[\text{Sn}^{2+}]_{\text{T}} = 10^{-4} \text{ M}$  and  $[\text{PO}_4^{3-}]_{\text{T}} = 10^{-3} \text{ M}$ . The diagram was calculated using the constants reported in [2000CIA/IUL2] and  $\text{p}K_1 = 1.86$ ,  $\text{p}K_2 = 6.26$  and  $\text{p}K_3 = 10.78$  for the dissociation constants of phosphoric acid [1969BAL/SIL], [1971PET]. The complexes with maximum concentration less than  $10^{-6} \text{ M}$  are not shown.

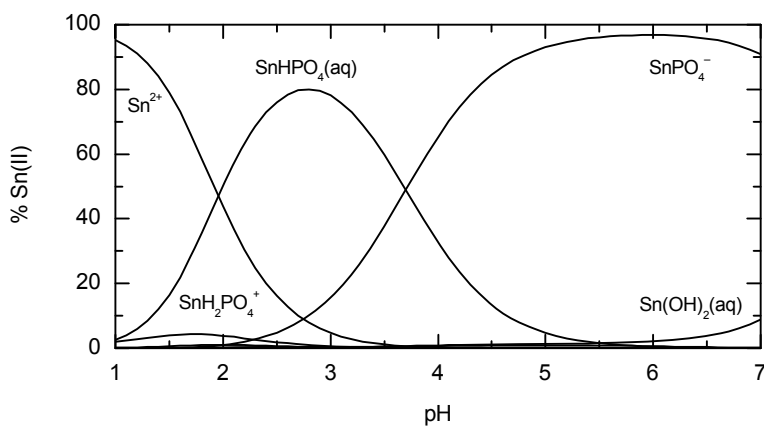


Table X-3: Experimental and calculated formation constants of the tin(II)-phosphato complexes.

Method	Ionic media	$t / ^\circ\text{C}$	$\log_{10} K$ reported	$\log_{10} K^\circ$ estimated <sup>(a)</sup>	Reference
$\text{Sn}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{SnH}_2\text{PO}_4^+$					
Ise-Sn, gl	3 M $\text{NaClO}_4$	25	$2.17 \pm 0.03$	$2.8 \pm 0.2$	[2000CIA/IUL2]
$\text{Sn}^{2+} + 2\text{H}_2\text{PO}_4^- \rightleftharpoons \text{Sn}(\text{H}_2\text{PO}_4)_2(\text{aq})$					
Ise-Sn, gl	3 M $\text{NaClO}_4$	25	$4.82 \pm 0.01$	$5.9 \pm 0.2$	[2000CIA/IUL2]

(Continued on next page)

Table X-3 (continued)

Method	Ionic media	$t / ^\circ\text{C}$	$\log_{10} K$ reported	$\log_{10} K^\circ$ estimated <sup>(a)</sup>	Reference
$\text{Sn}^{2+} + \text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} \rightleftharpoons \text{Sn}(\text{H}_2\text{PO}_4)(\text{HPO}_4)^-$					
Ise-Sn, gl	3 M NaClO <sub>4</sub>	25	$8.43 \pm 0.04^b$	$10.3 \pm 0.2$	[2000CIA/IUL2]
$\text{Sn}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{SnHPO}_4(\text{aq})$					
Ise-Sn, gl	3 M NaClO <sub>4</sub>	25	$7.55 \pm 0.01^b$	$9.5 \pm 0.2$	[2000CIA/IUL2]
sol	0.2 M NaClO <sub>4</sub>	25	$7.83 \pm 0.11$		[1968CIL]
$\text{Sn}^{2+} + 2\text{HPO}_4^{2-} \rightleftharpoons \text{Sn}(\text{HPO}_4)_2^{2-}$					
Ise-Sn, gl	3 M NaClO <sub>4</sub>	25	$13.88 \pm 0.03^b$	$13.4 \pm 0.2$	[2000CIA/IUL2]
$\text{Sn}^{2+} + 3\text{HPO}_4^{2-} \rightleftharpoons \text{Sn}(\text{HPO}_4)_3^{4-}$					
Ise-Sn, gl	3 M NaClO <sub>4</sub>	25	$12.68 \pm 0.01^b$	$12.9 \pm 0.2$	[2000CIA/IUL2]
sol	0.2 M NaClO <sub>4</sub>	25	$10.04 \pm 0.14$		[1968CIL]
$\text{Sn}^{2+} + \text{PO}_4^{3-} \rightleftharpoons \text{SnPO}_4^-$					
Ise-Sn, gl	3 M NaClO <sub>4</sub>	25	$14.63 \pm 0.01^b$	$18.0 \pm 0.2$	[2000CIA/IUL2]

(a) Extrapolated to  $I = 0$  by Ciavatta and Iuliano using the SIT approach and estimated ion interaction coefficients, see Appendix A.

(b) Calculated from the reported data using  $\text{p}K_1 = 1.86$ ,  $\text{p}K_2 = 6.26$  and  $\text{p}K_3 = 10.78$  for the dissociation constants of phosphoric acid [1969BAL/SIL], [1971PET].

### X.2.2.2 Aqueous tin(II) pyrophosphato complexes

As in the earlier volumes in this series, the only polyphosphate(V) species considered is the pyrophosphate (diphosphate). Other polyphosphoric acid species have negligible equilibrium concentrations at total phosphate concentrations  $< 0.045 \text{ mol}\cdot\text{dm}^{-3}$  and at temperatures below  $200^\circ\text{C}$  [1974MES/BAE]. The pyrophosphato complexes of tin(II) have been studied by potentiometric [1986TUR/KRA], [1986TUR/KRA2], [1991DUF/WIL], polarographic [1980ORE/AND], [1987TUR/KRA] and spectrophotometric [1980ORE/AND2] methods, as well as by solubility measurements [1966MES/IRA]. Only qualitative information is reported in [1966MES/IRA] and [1980ORE/AND]. For reasons mentioned in Appendix A, the equilibrium constants reported in [1980ORE/AND2] were not considered in this review. Although the highly charged pyrophosphate forms very stable complexes with tin(II), several factors complicate the interpretation of the experimental data. The alkali metal ions are known to form relatively stable complexes with pyrophosphate, especially above pH 8 where the species  $\text{P}_2\text{O}_7^{4-}$  is dominant in the solution [1994STE/FOT]. Therefore, the association constants of the pyrophosphate-alkali metal ion complexes (ion-pairs) should be considered, unless a sufficiently low concentration of the background electrolyte is used. This association is neglected in all publications dealing with the tin(II)-pyrophosphate interaction, and only one of them used relatively (but not

sufficiently) low ionic strength [1991DUF/WIL], therefore the reported equilibrium constants can be regarded only as conditional/apparent stability constants.

In addition, a great variety of complexes are reported in the literature depending on the metal-to-ligand ratio and pH, and their unambiguous identification is a rather difficult task. The experimental data obtained for the tin(II)-pyrophosphate interaction were discussed in terms of the following generalised equilibrium involving 13 individual species (Table X-4):

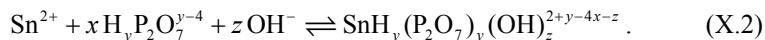


Table X-4: Experimental equilibrium constants<sup>(a)</sup> for the processes  $\text{Sn}^{2+} + x\text{H}_y\text{P}_2\text{O}_7^{y-4} + z\text{OH}^- \rightleftharpoons \text{SnH}_y(\text{P}_2\text{O}_7)_x(\text{OH})_z^{2+y-4x-z}$ .

(x,y,z)	method	ionic medium	log <sub>10</sub> K <sub>x,y,z</sub> reported	log <sub>10</sub> K <sub>x,y,z</sub> recalculated	Reference
(1,2,0)	vol	1 M NaClO <sub>4</sub>	4.73 ± 0.08		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	4.74 ± 0.06	–	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	3.20 ± 0.05		[1980ORE/AND2]
(1,1,0)	vol	1 M NaClO <sub>4</sub>	8.57 ± 0.10		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	8.55 ± 0.08	8.64 ± 0.06	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	9.26 ± 0.08		[1980ORE/AND2]
(1,0,0)	gl	0.15 M NaCl	12.05 ± 0.11		[1991DUF/WIL]
	vol	1 M NaClO <sub>4</sub>	13.07 ± 0.10		[1987TUR/KRA]
	Ise-Sn, gl, vol	1 M NaClO <sub>4</sub>	13.05 ± 0.10	12.78 ± 0.05	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	14.30 ± 0.05		[1980ORE/AND2]
(1,0,1)	gl	0.15 M NaCl	19.68 ± 0.15		[1991DUF/WIL]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	19.32 ± 0.10	18.66 ± 0.09	Tur'yan <i>et al.</i> <sup>(b)</sup>
(1,0,2)	Ise-Sn, gl	1 M NaClO <sub>4</sub>	23.39 ± 0.06	23.33 ± 0.04	Tur'yan <i>et al.</i> <sup>(b)</sup>
(2,4,0)	vol	1 M NaClO <sub>4</sub>	6.13 ± 0.09		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	6.11 ± 0.08	–	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	6.98 ± 0.02		[1980ORE/AND2]
(2,3,0)	gl	0.15 M NaCl	9.96 ± 0.17		[1991DUF/WIL]
	vol	1 M NaClO <sub>4</sub>	10.00 ± 0.09		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	9.97 ± 0.08	9.70 ± 0.14	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	10.58 ± 0.05		[1980ORE/AND2]
(2,2,0)	gl	0.15 M NaCl	12.02 ± 0.22		[1991DUF/WIL]
	vol	1 M NaClO <sub>4</sub>	12.10 ± 0.10		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	12.07 ± 0.06	11.74 ± 0.14	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	15.04 ± 0.03 <sup>(c)</sup>		[1980ORE/AND2]
(2,1,0)	gl	0.15 M NaCl	14.54 ± 0.20		[1991DUF/WIL]

(Continued on next page)

Table X-4 (continued)

(x,y,z)	method	ionic medium	log <sub>10</sub> K <sub>x,y,z</sub> reported	log <sub>10</sub> K <sub>x,y,z</sub> recalculated	Reference
	vol	1 M NaClO <sub>4</sub>	14.95 ± 0.09		[1987TUR/KRA]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	14.94 ± 0.03	14.67 ± 0.05	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	14.45 ± 0.04		[1980ORE/AND2]
(2,0,0)	gl	0.15 M NaCl	15.48 ± 0.26		[1991DUF/WIL]
	Ise-Sn, gl	1 M NaClO <sub>4</sub>	16.27 ± 0.02	16.13 ± 0.02	Tur'yan <i>et al.</i> <sup>(b)</sup>
	spe	0.333 M K <sub>2</sub> SO <sub>4</sub>	16.48 ± 0.05		[1980ORE/AND2]
(2,0,1)	Ise-Sn, gl	1 M NaClO <sub>4</sub>	21.04 ± 0.04	21.09 ± 0.03	Tur'yan <i>et al.</i> <sup>(b)</sup>
(3,0,0)	gl	0.15 M NaCl	18.40 ± 0.21		[1991DUF/WIL]

- (a) The protonation constants of pyrophosphate for  $I = 0.15$  M NaCl:  $\log_{10} \beta_{1,1} = (8.14 \pm 0.01)$ ,  $\log_{10} \beta_{1,2} = (14.01 \pm 0.01)$ ,  $\log_{10} \beta_{1,3} = (15.78 \pm 0.02)$ ,  $\log_{10} \beta_{1,4} = (16.63 \pm 0.10)$  (determined in [1991DUF/WIL],  $pK_w = 13.71$ ); for  $I = 1$  M NaClO<sub>4</sub>:  $\log_{10} \beta_{1,1} = 7.36$ ,  $\log_{10} \beta_{1,2} = 11.72$ ,  $\log_{10} \beta_{1,3} = 14.12$ ,  $\log_{10} \beta_{1,4} = 14.87$  (taken from [1968BOT/CIA],  $pK_w = 13.80$ ).
- (b) Average values of the constants reported in [1986TUR/KRA], [1986TUR/KRA2] and [1987TUR/KRA]. The re-evaluation was based on the combined datasets of the two papers. The formation constants of the binary hydroxido complexes were calculated from the selected values.
- (c) Two isomers are reported, the individual constants are  $\log_{10} K = (12.28 \pm 0.03)$  and  $(14.95 \pm 0.02)$  for the complexes  $\text{Sn}(\text{HP}_2\text{O}_7)_2^{4-}$  and  $\text{Sn}(\text{P}_2\text{O}_7)(\text{HP}_2\text{O}_7)^+$ , respectively.

The re-evaluation of the experimental data reported in [1986TUR/KRA] and [1986TUR/KRA2] justified only the formation of 9 of the 11 reported species (the complexes  $\text{SnH}_2(\text{P}_2\text{O}_7)(\text{aq})$  and  $\text{SnH}_4(\text{P}_2\text{O}_7)_2^{2-}$  were rejected, see Appendix A). Six of them were identified in [1991DUF/WIL], too, indicating significant overlap between the equilibrium models. However, the speciation based on the re-evaluated data of Tur'yan *et al.* is rather different from that suggested in [1991DUF/WIL] (see Figure X-3), which is at least in part due to the neglected interaction of pyrophosphate ions with sodium ion.

### X.2.2.3 Aqueous tin(IV) pyrophosphato complexes

The highly charged pyrophosphate anion forms very stable complexes with tin(IV), which suppress the formation of  $\text{SnO}_2(\text{s})$  in the whole pH range. Duffield *et al.* reported [1991DUF/WIL] the presence of five complexes ( $\text{SnHP}_2\text{O}_7^+$ ,  $\text{SnP}_2\text{O}_7(\text{aq})$ ,  $\text{SnH}(\text{P}_2\text{O}_7)_2^{3-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_2^{4-}$  and  $\text{Sn}(\text{P}_2\text{O}_7)(\text{OH})_2^{6-}$ ) between pH 1 and 8, based on their pH-metric study (Table X-5). Note, that protonation isomers (*e.g.*  $\text{SnP}_2\text{O}_7(\text{aq})$  and  $\text{Sn}(\text{HP}_2\text{O}_7)(\text{OH})(\text{aq})$ ) cannot be distinguished by pH-metry. The formation of  $\text{Sn}(\text{P}_2\text{O}_7)_2^{4-}$  around pH 6 is also supported by the  $^{31}\text{P} - ^{119}\text{Sn}$  spin-spin coupling pattern observed by  $^{119}\text{Sn}$  NMR spectroscopy [1986MAT/THI]. In case of strongly hydrolyzing metal ions, the hydroxido complexes should be involved in the equilibrium model.

However, Duffield *et al.* considered only the formation of  $\text{Sn}(\text{OH})^{3+}$  and  $\text{Sn}(\text{OH})_6^{2-}$ , disregarding *e.g.* the complex  $\text{Sn}(\text{OH})_5^-$ . Therefore, the equilibrium constants reported in [1991DUF/WIL] cannot be used to calculate selected values.

Table X-5: Experimental formation constants\* for the processes  $p\text{Sn}^{4+} + q\text{P}_2\text{O}_7^{4-} + r\text{H}^+ \rightleftharpoons \text{Sn}_p\text{H}_r(\text{P}_2\text{O}_7)_q^{4p-4q+r}$  obtained from pH-metric measurements by [1991DUF/WIL] ( $I = 0.15 \text{ M NaCl}$ ,  $T = 298 \text{ K}$ ).

$pqr$	$\log_{10} \beta_{pqr}$
111	$23.56 \pm 0.42$
110	$22.61 \pm 0.27$
121	$33.36 \pm 0.06$
120	$27.08 \pm 0.09$
12-1	$19.84 \pm 0.12$

\* The protonation constants of pyrophosphate determined by the authors:  $\log_{10} \beta_{11} = (8.14 \pm 0.01)$ ,  $\log_{10} \beta_{12} = (14.01 \pm 0.01)$ ,  $\log_{10} \beta_{13} = (15.78 \pm 0.02)$ ,  $\log_{10} \beta_{14} = (16.63 \pm 0.10)$ ; the formation constant of the hydroxo complexes considered in the data evaluation:  $\log_{10} \beta_{10,1} = -1.937$ ,  $\log_{10} \beta_{10,6} = -24.108$ .

## X.3 Arsenic compounds and complexes

### X.3.1 Tin arsenides

In the binary system Sn-As, two intermediate phases SnAs and  $\text{Sn}_4\text{As}_3$  are known.

The thermodynamic data in this system are described by Gladyshev and Pashkov [1978GLA/PAS], Koshchenko *et al.* [1980KOS/PAS2] and Fitzner and Kleppa [1996FIT/KLE].

#### X.3.1.1 SnAs(cr)

Fitzner and Kleppa [1996FIT/KLE] used direct synthesis drop calorimetry in fused silica capsules to measure the standard enthalpy of formation of several binary alloy compositions in the systems Si-As, Ge-As and Sn-As.

The standard enthalpy of formation of SnAs(cr) determined by this method is

$$\Delta_f H_m^\circ(\text{SnAs, cr, 298.15 K}) = -(9.5 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selected value is in very good agreement with the one recommended by Gokcen ( $-11.3 \text{ kJ}\cdot\text{mol}^{-1}$ ) in his recent assessment of the As-Sn system [1990GOK].

Koshchenko *et al.* [1980KOS/PAS2] measured the data from a temperature of 5.73 to 313 K (see Appendix A). In the integration of the data in Table X-6, the superconducting phase transition at 3.7 K was not considered. The errors of measurements are 1.5% in the range from 5 to 40 K and 0.5% from 40 K and above. The experimental data and the fit functions are depicted in Figure X-4.

Table X-6: Thermodynamic properties of SnAs(cr). Smoothed and numerically integrated data of Koshchenko *et al.* [1980KOS/PAS2]. Values in parentheses have been recalculated by fit functions, see Appendix A entry for [1980KOS/PAS2].

$T/K$	$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H(T) - H(0\text{K}) / \text{J}\cdot\text{mol}^{-1}$	$S_m^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-[(G(T) - G(0\text{K}))T^{-1}] / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
5.00	0.070 (0.0417)	0.176 (0.0522)	0.0233 (0.0139)	-0.0119 (0.0035)
10.00	0.418 (0.450)	1.40 (0.73)	0.233 (0.091)	0.093 (0.019)
15.00	2.15 (2.318)	7.82 (7.05)	0.75 (0.579)	0.229 (0.109)
20.00	5.10 (5.260)	25.9 (25.70)	1.78 (1.632)	0.485 (0.347)
25.00	8.48 (8.599)	59.9 (60.29)	3.29 (3.161)	0.89 (0.750)
30.00	11.8 (11.934)	111 (111.67)	5.14 (5.026)	1.44 (1.303)
35.00	14.4 (15.082)	176 (179.31)	7.15 (7.105)	2.12 (1.982)
40.00	18.1 (18.081)	257 (262.06)	9.32 (9.311)	2.90 (2.759)
45.00	21.1 (21.046)	355 (360.07)	11.62 (11.617)	3.73 (3.615)
50.00	23.9 (23.898)	468 (472.49)	13.99 (13.983)	4.63 (4.533)
60.00	29.0 (28.954)	734 (737.59)	18.83 (18.802)	6.52 (6.509)
70.00	32.9 (32.988)	1044 (1048.12)	23.60 (23.581)	8.48 (8.608)
80.00	36.1 (36.145)	1390 (1394.43)	28.2 (28.201)	10.54 (10.770)
90.00	38.6 (38.620)	1764 (1768.74)	32.6 (32.606)	12.64 (12.954)
100.00	40.6 (40.578)	2160 (2165.10)	36.8 (36.781)	14.75 (15.130)
110.00	42.1 (42.147)	2570 (2579.01)	40.7 (40.725)	16.84 (17.279)
120.00	43.3 (43.420)	3000 (3007.07)	44.4 (44.448)	18.91 (19.389)
130.00	44.4 (44.466)	3440 (3446.67)	47.9 (47.966)	20.93 (21.454)
140.00	45.3 (45.337)	3890 (3895.81)	51.3 (51.295)	22.91 (23.467)
150.00	46.0 (46.071)	4340 (4352.95)	54.4 (54.448)	24.92 (25.428)
160.00	46.7 (46.699)	4810 (4816.88)	57.4 (57.442)	26.73 (27.337)
170.00	47.3 (47.242)	5270 (5286.64)	60.3 (60.290)	28.5 (29.192)
180.00	47.7 (47.718)	5750 (5761.49)	63.0 (63.004)	30.3 (30.996)
190.00	48.1 (48.140)	6230 (6240.81)	65.6 (65.595)	32.1 (32.749)
200.00	48.5 (48.520)	6710 (6724.15)	68.0 (68.074)	33.7 (34.454)
220.00	49.2 (49.186)	7690 (7701.39)	72.7 (72.731)	37.0 (37.725)
240.00	49.8 (49.764)	8680 (8691.00)	77.0 (77.036)	40.1 (40.823)

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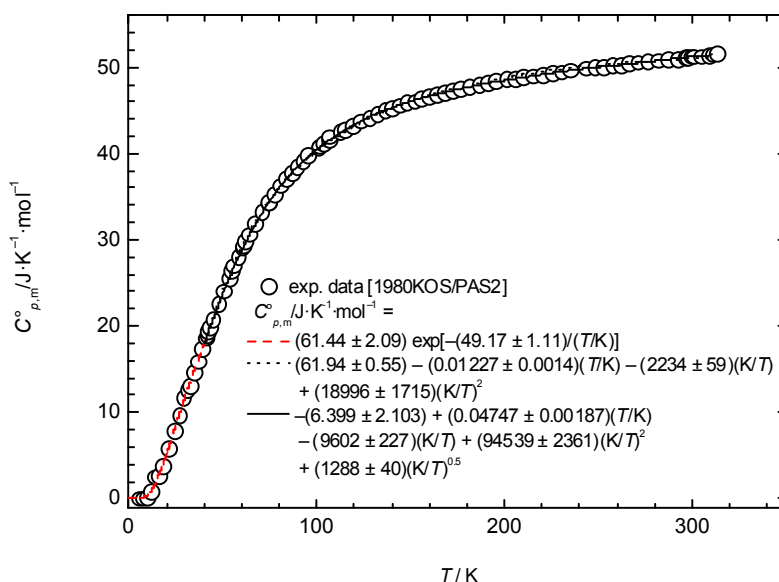
Table X-6 (continued)

$T/K$	$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H(T) - H(0\text{K}) / \text{J}\cdot\text{mol}^{-1}$	$S_m^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-[(G(T) - G(0\text{K}))T^{-1}] / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
260.00	50.2 (50.286)	9680 (9691.57)	81.0 (81.040)	43.0 (43.765)
273.15	50.6 (50.610)	10300 (10354.98)	83.5 (83.529)	44.8 (45.620)
290.00	51.0 (51.012)	11200 (11211.16)	86.5 (86.571)	47.1 (47.911)
298.15	51.2 (51.202)	11600 (11627.68)	88.0 (87.987)	48.2 (48.988)
310.00	51.5 (51.477)	12200 (12236.06)	90.0 (89.988)	50.0 (50.517)

Figure X-4: Heat capacity data of SnAs(cr) as measured by Koshchenko *et al.* [1980KOS/PAS2]. The data can be fitted using the equations:

$$[C_{p,m}^{\circ}]_{15\text{K}}^{40\text{K}}(\text{SnAs, cr, } T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (61.44 \pm 2.09) \exp[-(49.17 \pm 1.11)/(T/K)] \text{ and}$$

$$[C_{p,m}^{\circ}]_{140\text{K}}^{313\text{K}}(\text{SnAs, cr, } T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -(6.399 \pm 2.103) + (0.04747 \pm 0.00187)(T/K) - (9602 \pm 227)/(T/K) + (94539 \pm 2361)/(T/K)^2 + (1288 \pm 40)/(T/K)^{0.5}.$$



The selected data are:

$$C_{p,m}^{\circ}(\text{SnAs, cr, } 298.15 \text{ K}) = (51.2 \pm 0.26) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{SnAs, cr, } 298.15 \text{ K}) = (88.0 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^{\circ}(\text{SnAs, cr, } 298.15 \text{ K}) = -(9.5 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_f G_m^{\circ}(\text{SnAs, cr, 298.15 K}) = - (10.0 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

### X.3.1.2 Sn<sub>4</sub>As<sub>3</sub>(cr)

Koshchenko *et al.* [1980KOS/PAS], [1980KOS/DEM] measured the heat capacity of solid solutions in the system Sn-As with 57 to 60% Sn close to the composition Sn<sub>4</sub>As<sub>3</sub> in the temperature range 5.5 to 310 K. The measurement errors are similar to those for SnAs, namely 1.5% between 5 and 40 K and 0.5% above 40 K. Two different compositions were used with  $w(\text{Sn}) = 0.58$  and 0.59; the difference in the heat capacity between the two compositions was approximately 1.2%. The numerically integrated data for the  $w(\text{Sn}) = 0.58$  and the 0.59 compound are reported in Table X-7 and Table X-8 respectively, and compared with appropriate fit functions in Figure X-5.

Table X-7: Thermodynamic properties of Sn<sub>3</sub>As<sub>4</sub>. Smoothed and numerically integrated data on Sn<sub>4</sub>As<sub>3</sub> with 58% Sn. Values in parentheses have been recalculated by modified fit functions, see Appendix A entry for [1980KOS/PAS].

$T/\text{K}$	$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H(T) - H(0\text{K}) / \text{J}\cdot\text{mol}^{-1}$	$S_m^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-[(G(T) - G(0\text{K}))T^{-1}] / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
5.00	0.381 (0.433)	0.88 (0.541)	0.127 (0.144)	-0.049 (0.036)
10.00	4.60 (3.860)	13.3 (8.368)	2.04 (1.072)	0.71 (0.235)
15.00	15.6 (14.646)	63.7 (53.939)	6.07 (4.625)	1.82 (1.029)
20.00	27.5 (27.131)	171 (158.184)	12.2 (10.537)	3.67 (2.628)
25.00	38.5 (39.274)	336 (324.587)	19.6 (17.913)	6.12 (4.930)
30.00	49.2 (50.258)	556 (548.958)	27.5 (26.064)	9.0 (7.765)
35.00	60.0 (59.938)	828 (824.981)	35.9 (34.555)	12.2 (10.984)
40.00	69.9 (69.320)	1153 (1146.310)	44.6 (43.123)	15.8 (14.465)
45.00	79.1 (79.149)	1526 (1519.363)	53.9 (51.901)	20.0 (18.137)
50.00	88.0 (88.271)	1944 (1937.992)	62.1 (60.713)	23.3 (21.953)
60.00	105.5 (104.694)	2920 (2905.318)	79.8 (78.304)	30.5 (29.882)
70.00	117.8 (117.911)	4030 (4020.894)	97.0 (95.475)	37.7 (38.034)
80.00	128.0 (128.283)	5260 (5253.920)	113 (111.924)	45.1 (46.250)
90.00	136.2 (136.425)	6590 (6579.026)	129 (127.522)	55.778 (54.422)
100.00	143.1 (142.875)	7980 (7976.699)	144 (142.242)	64.200 (62.475)
110.00	148.0 (148.045)	9440 (9432.176)	158 (156.111)	72.182 (70.364)
120.00	152.2 (152.247)	10900 (10934.296)	171 (169.178)	80.167 (78.059)
130.00	155.6 (155.709)	12500 (12474.571)	183 (181.505)	86.846 (85.547)

(Continued on next page)



Table X-7 (continued)

$T/K$	$C_{p,m}^o / J \cdot K^{-1} \cdot mol^{-1}$		$H(T) - H(0K) / J \cdot mol^{-1}$		$S_m^o / J \cdot K^{-1} \cdot mol^{-1}$		$-[(G(T) - G(0K))T^{-1}] / J \cdot K^{-1} \cdot mol^{-1}$	
140.00	158.4	(158.603)	14000	(14046.506)	195	(193.153)	95.000	(92.821)
150.00	160.9	(161.057)	15600	(15645.090)	206	(204.181)	102.000	(99.880)
160.00	163.4	(163.169)	17300	(17266.436)	216	(214.644)	107.875	(106.729)
170.00	165.4	(165.013)	18900	(18907.509)	226	(224.593)	114.824	(113.372)
180.00	166.9	(166.647)	20600	(20565.933)	236	(234.071)	121.556	(119.816)
190.00	168.7	(168.116)	22300	(22239.840)	245	(243.121)	127.632	(126.069)
200.00	170.2	(169.455)	23900	(23927.759)	253	(251.779)	133.500	(132.140)
220.00	171.6	(171.847)	27400	(27341.256)	270	(268.044)	145.455	(143.766)
240.00	173.7	(173.987)	30800	(30799.864)	285	(283.090)	156.667	(154.757)
260.00	175.7	(175.977)	34300	(34299.634)	299	(297.095)	167.077	(165.173)
273.15	177.2	(177.239)	36600	(36622.027)	308	(305.809)	174.008	(171.736)
290.00	178.7	(178.827)	39600	(39621.873)	318	(316.465)	181.448	(179.838)
298.15	179.6	(179.590)	41100	(41082.403)	323	(321.432)	185.150	(183.641)
310.00	180.7	(180.697)	43200	(43217.072)	330	(328.453)	190.645	(189.043)

Table X-8: Thermodynamic properties of  $Sn_3As_4$ . Smoothed and numerically integrated data on  $Sn_4As_3$  with 59% Sn. Values in parentheses have been recalculated by modified fir functions, see Appendix a entry for [1980KOS/PAS].

$T/K$	$C_{p,m}^o / J \cdot K^{-1} \cdot mol^{-1}$		$H(T) - H(0K) / J \cdot mol^{-1}$		$S_m^o / J \cdot K^{-1} \cdot mol^{-1}$		$-[(G(T) - G(0K))T^{-1}] / J \cdot K^{-1} \cdot mol^{-1}$	
5	0.439	(0.710)	1.10	(0.888)	0.146	(0.237)	-0.074	(0.060)
10	5.30	(5.509)	15.4	(11.606)	2.35	(1.519)	0.81	(0.358)
15	19.2	(17.053)	72.7	(66.576)	6.94	(5.818)	2.09	(1.380)
20	30.2	(30.003)	192	(184.289)	13.8	(12.502)	4.16	(3.288)
25	40.7	(42.109)	370	(365.112)	21.7	(20.521)	6.86	(5.917)
30	51.1	(52.785)	599	(602.964)	30.0	(29.165)	10.0	(9.066)
35	61.4	(62.032)	881	(890.571)	38.7	(38.014)	13.5	(12.569)
40	71.3	(71.134)	1212	(1221.171)	47.5	(46.831)	17.2	(16.302)
45	80.9	(80.408)	1593	(1602.031)	56.4	(55.793)	21.0	(20.192)
50	90.0	(89.111)	2020	(2025.879)	65.4	(64.716)	25.0	(24.198)
60	104.6	(105.063)	3000	(2999.014)	83.3	(82.414)	32.5	(32.430)
70	118.3	(118.073)	4120	(4117.157)	100.6	(99.624)	41.743	(40.807)
80	128.4	(128.370)	5350	(5351.404)	117	(116.090)	50.125	(49.197)
90	136.5	(136.505)	6680	(6677.354)	133	(131.698)	58.778	(57.505)
100	143.1	(142.984)	8080	(8075.999)	147	(146.428)	66.200	(65.668)

(Continued on next page)

Table X-8 (continued)

$T/K$	$C_{p,m}^{\circ} / J \cdot K^{-1} \cdot mol^{-1}$	$H(T) - H(0K) / J \cdot mol^{-1}$	$S_m^{\circ} / J \cdot K^{-1} \cdot mol^{-1}$	$-[(G(T) - G(0K))T^{-1}] / J \cdot K^{-1} \cdot mol^{-1}$
110	148.4 (148.203)	9530 (9532.847)	161 (160.310)	74.364 (73.648)
120	152.8 (152.462)	11000 (11036.867)	174 (173.394)	82.333 (81.420)
130	156.2 (155.984)	12600 (12579.630)	187 (185.740)	90.077 (88.974)
140	159.1 (158.937)	14200 (14154.650)	198 (197.411)	96.571 (96.306)
150	161.4 (161.448)	15800 (15756.902)	209 (208.464)	103.667 (103.418)
160	163.4 (163.614)	17400 (17382.468)	220 (218.955)	111.250 (110.315)
170	165.5 (165.508)	19000 (19028.276)	230 (228.932)	118.235 (117.001)
180	167.2 (167.186)	20700 (20691.904)	239 (238.440)	124.000 (123.485)
190	168.9 (168.696)	22400 (22371.440)	248 (247.521)	130.105 (129.777)
200	170.2 (170.070)	24100 (24065.367)	257 (256.209)	136.500 (135.882)
220	172.3 (172.521)	27500 (27491.839)	273 (272.536)	148.000 (147.573)
240	174.5 (174.702)	31000 (30964.415)	289 (287.643)	159.833 (158.626)
260	176.6 (176.719)	34500 (34478.833)	303 (301.707)	170.308 (169.096)
273.15	178.0 (177.991)	36800 (36811.088)	311 (310.457)	174.008 (175.692)
290	179.8 (179.584)	39800 (39823.704)	322 (321.159)	184.759 (183.836)
298.15	180.5 (180.346)	41300 (41290.423)	327 (326.147)	188.479 (187.658)
310	181.6 (181.450)	43400 (43434.068)	334 (333.197)	194.000 (193.087)

The data can be fitted by the following equations:

$$[C_{p,m}^{\circ}]_{15K}^{40K}(\text{Sn}_4\text{As}_3, \text{cr}, T) / J \cdot K^{-1} \cdot mol^{-1} = (167.9 \pm 3.9) \exp[-(35.55 \pm 0.70)/(T/K)]$$

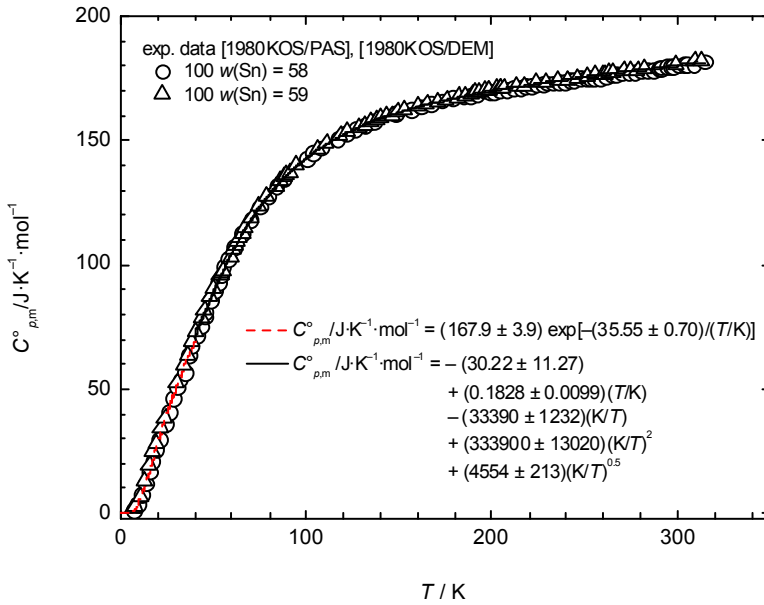
$$[C_{p,m}^{\circ}]_{140K}^{315K}(\text{Sn}_4\text{As}_3, \text{cr}, T) / J \cdot K^{-1} \cdot mol^{-1} = - (30.22 \pm 11.26) + (0.1828 \pm 0.0099) T/K \\ - (33393 \pm 1232)/(T/K) \\ + (333880 \pm 13018)/(T/K)^2 \\ + (4554 \pm 213)/(T/K)^{0.5}.$$

The selected data for  $\text{Sn}_4\text{As}_3(\text{cr})$  are:

$$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr}, 298.15 \text{ K}) = (179.8 \pm 0.6) J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m^{\circ}(\text{Sn}_4\text{As}_3, \text{cr}, 298.15 \text{ K}) = (323.8 \pm 3.8) J \cdot K^{-1} \cdot mol^{-1}.$$

Figure X-5: Two sets of measured heat capacity data for  $\text{Sn}_4\text{As}_3$  with  $w(\text{Sn}) = 0.58$  and  $0.59$  [1980KOS/PAS]. The difference between the two  $C_{p,m}^\circ$  data sets is about 1.2% through the whole range.





# Chapter XI

## Group 14 compounds and complexes

### XI.1 Aqueous tin thiocyanato complexes

#### XI.1.1 Aqueous Sn(II) thiocyanates

The formation of thiocyanato complexes of tin(II) in aqueous solution has been reported in [1961GOL/OGN], [1976SAM/LYA] and [1980FED/BOL]. The equilibrium constants for the reactions



are summarised in Table XI-1.

Table XI-1: Experimental formation constants of the species  $\text{SnSCN}_q^{2-q}$ .

Method	Ionic media	$t / ^\circ\text{C}$	$\log_{10} \beta_q$			Reference
			reported	Recalculated <sup>(a)</sup>	Accepted <sup>(b)</sup>	
$\text{Sn}^{2+} + \text{SCN}^- \rightleftharpoons \text{SnSCN}^+$						
Ise-Sn	2.2 M NaClO <sub>4</sub>	20	1.17	0.70 ± 0.01	0.65 ± 0.30	[1961GOL/OGN]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	1.03 ± 0.07			[1976SAM/LYA]
Ise-Sn	0.5 M NaClO <sub>4</sub>	25	1.32 ± 0.02			[1980FED/BOL]
	1.0 M NaClO <sub>4</sub>	25	0.83 ± 0.06		0.81 ± 0.50	
	3.0 M NaClO <sub>4</sub>	25	0.90 ± 0.10		0.83 ± 0.50	
$\text{Sn}^{2+} + 2 \text{SCN}^- \rightleftharpoons \text{Sn}(\text{SCN})_2(\text{aq})$						
Ise-Sn	2.2 M NaClO <sub>4</sub>	20	1.77	1.65 ± 0.01	1.55 ± 0.30	[1961GOL/OGN]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	1.57 ± 0.03			[1976SAM/LYA]
Ise-Sn	1.0 M NaClO <sub>4</sub>	25	1.10 ± 0.10			[1980FED/BOL]
	3.0 M NaClO <sub>4</sub>	25	1.40 ± 0.10			
$\text{Sn}^{2+} + 3 \text{SCN}^- \rightleftharpoons \text{SnSCN}_3^-$						
Ise-Sn	2.2 M NaClO <sub>4</sub>	20	1.72			[1961GOL/OGN]
Ise-Sn	3.0 M NaClO <sub>4</sub>	25	1.53 ± 0.10			[1980FED/BOL]

(a) Re-evaluated values, see Appendix A.

(b) Accepted values converted to molal scale. The accepted values reported in Appendix A are expressed on the molar or molal scales, depending on which units were used originally by the authors.

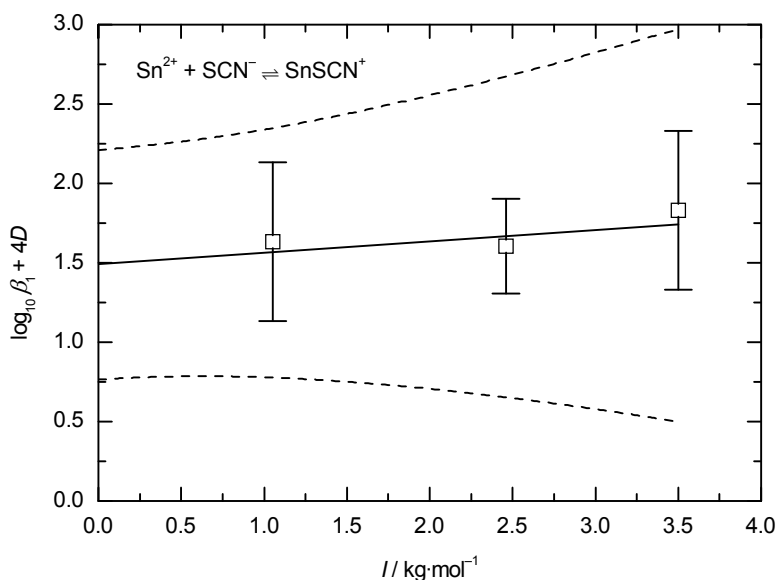
For reasons mentioned in Appendix A, the constants reported in [1976SAM/LYA] were not considered in this review. The re-evaluation of the potentiometric data of [1961GOL/OGN] determined at 293.15 K indicated that the consideration of two species ( $\text{SnSCN}^+$  and  $\text{Sn}(\text{SCN})_2(\text{aq})$ ) is sufficient to describe the experimental data up to 20% replacement of the background electrolyte (at higher thiocyanate concentrations a notable medium effect may arise). The temperature correction to 298.15 K is assumed to be negligible. The constants for Reaction ((XI.1),  $q = 2$  and 3) reported in [1980FED/BOL] were not considered, since these reactions take place in a region where an important medium effect can be expected. Similarly, the value of  $\log_{10} \beta_1$  reported in [1980FED/BOL] for  $I = 0.5 \text{ M}$  was rejected, as the amount of  $\text{SnSCN}^+$  formed up to  $[\text{SCN}^-]_{\text{tot}} = 0.1 \text{ M}$  (20% replacement of the background electrolyte) is probably too small to produce a reliable value.

The SIT analysis of the remaining 3 values (Figure XI-1) resulted in the following selected constant

$$\log_{10} \beta_1^{\circ} ((\text{XI.1}), q = 1, 298.15 \text{ K}) = (1.5 \pm 0.7).$$

The corresponding ion interaction coefficient is  $\Delta \varepsilon((\text{XI.1}), q = 1) = -(0.07 \pm 0.29) \text{ kg}\cdot\text{mol}^{-1}$ .

Figure XI-1: Extrapolation to  $I = 0$  of the experimental data for reaction  $\text{Sn}^{2+} + \text{SCN}^- \rightleftharpoons \text{SnSCN}^+$  in  $\text{NaClO}_4$  media. Experimental data from [1961GOL/OGN] and [1980FED/BOL].



The selected thermodynamic formation constant corresponds to

$$\Delta_f G_m^\circ ((\text{XI.1}), q = 1, 298.15 \text{ K}) = - (8.6 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The Gibbs energy of formation is calculated using the selected values for  $\text{Sn}^{2+}$  and  $\text{SCN}^-$ :

$$\Delta_f G_m^\circ (\text{SnSCN}^+, 298.15 \text{ K}) = (56.7 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}.$$





## **Part 4**

# **Appendices**



# Appendix A

## Discussion of selected references

This appendix comprises discussions relating to a number of key publications which contain experimental information cited in this review. These discussions are fundamental in explaining the accuracy of the data concerned and the interpretation of the experiments, but they are too lengthy or are related to too many different sections to be included in the main text. The notation used in this appendix is consistent with that used in the present book, and not necessarily consistent with that used in the publication under discussion.

### [1813BER]

In this paper among other things the preparation and analysis of black tin(II) oxide was reported. The first stage was to precipitate white, hydrous tin(II) oxide from tin(II) chloride solutions with potassium carbonate.

### [1844SCH]

On pages 174 and 175 preparations and analyses of tin(II) oxide hydrate and tin(IV) oxide hydrate are reported.

Tin(II) oxide hydrate was obtained by precipitating tin(II) chloride solutions with potassium carbonate solutions. After drying at 80 °C in a stream of carbon dioxide the substance contained 93.54% SnO and 6.46% H<sub>2</sub>O apparently conforming to 2SnO·H<sub>2</sub>O (theor. 93.73% SnO and 6.27% H<sub>2</sub>O).

### [1882DIT]

This is a short communication reporting the syntheses of basic tin(II) chlorides: SnCl<sub>2</sub>·4SnO·6H<sub>2</sub>O, 2SnCl<sub>2</sub>·3SnO·6H<sub>2</sub>O, and SnCl<sub>2</sub>·SnO·4H<sub>2</sub>O. Detailed analyses of these products are given in [1882DIT2].

### [1882DIT2]

In this paper the syntheses and analyses of two tin(II) oxide hydrates, three basic tin(II) chlorides and two basic tin(II) sulfates were reported.

Tin(II) oxide hydrates:

- 1)  $\text{SnO} \cdot 2.23\text{H}_2\text{O} \hat{=} \text{SnO} \cdot 2\text{H}_2\text{O}^1$
- 2)  $\text{SnO} \cdot 0.73\text{H}_2\text{O} \hat{=} 3\text{SnO} \cdot 2\text{H}_2\text{O}$

Basic tin(II) chlorides:

- 1)  $\text{SnCl}_{0.39}\text{O}_{0.79} \cdot 1.14\text{H}_2\text{O} \hat{=} \text{SnCl}_2 \cdot 4\text{SnO} \cdot 6\text{H}_2\text{O}$
- 2)  $\text{SnCl}_{0.79}\text{O}_{0.61} \cdot 1.23\text{H}_2\text{O} \hat{=} 2\text{SnCl}_2 \cdot 3\text{SnO} \cdot 6\text{H}_2\text{O}$
- 3)  $\text{SnCl}_{1.00}\text{O}_{0.50} \cdot 1.92\text{H}_2\text{O} \hat{=} \text{SnCl}_2 \cdot \text{SnO} \cdot 4\text{H}_2\text{O}$

Basic tin(II) sulfates:

- 1)  $\text{Sn}_3\text{O}_{1.99}(\text{SO}_4)_{1.01} \cdot 1.04\text{H}_2\text{O} \hat{=} \text{Sn}_3(\text{OH})_2\text{OSO}_4$
- 2)  $\text{Sn}_3\text{O}_{1.98}(\text{SO}_4)_{1.02} \hat{=} \text{Sn}_3\text{O}_2\text{SO}_4$

The methods used in analysing the substances were not reported. The stoichiometric formula of the only crystallised tin(II) hydroxide oxide turned out to be  $3\text{SnO} \cdot \text{H}_2\text{O}$  [1968HOW/MOS], thus Ditte's analyses reflect the difficulty to remove adhering water from the precipitated product completely.

It turned out that hydrolysis of tin(II) in aqueous, chloride containing solutions gives abhurite,  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  as the sole well crystallised solid phase at low pH. Thus the solids obtained by Ditte's synthetic procedures are probably mixtures of abhurite and tin(II) hydroxide oxide or tin(II) chloride oxide [1981SCH/NES], [1992EDW/GIL].

The basic tin(II) sulfate,  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ , is indeed a corrosion product found on the surfaces of tin and its alloys.

### [1897YOU]

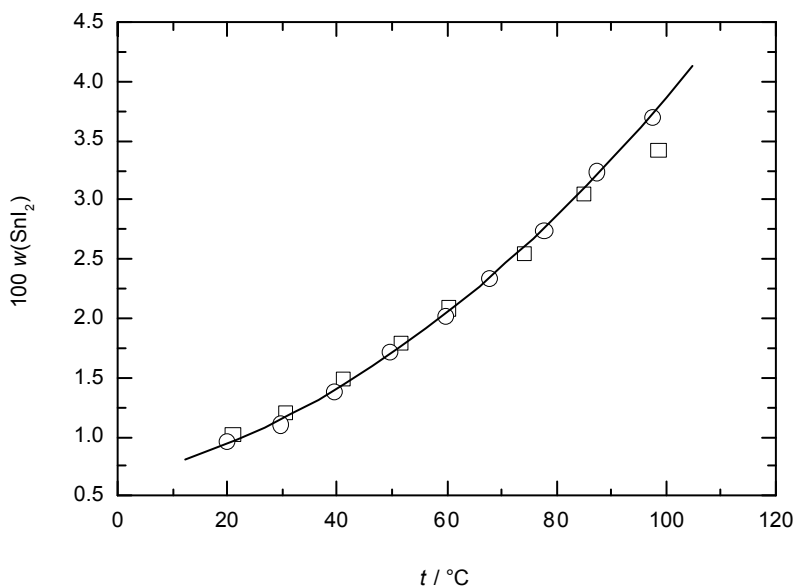
In preparation of  $\text{SnI}_2$  partly formed  $\text{SnI}_4$  was extracted by  $\text{CS}_2$  and  $\text{SnI}_2$  stored in  $\text{CS}_2$ .  $\text{SnI}_2(\text{s})$  was stirred in a  $100 \text{ cm}^3$  test tube with solvent. After heating to near boiling the tube was put into a beaker with water. Temperature was read from an inserted thermometer inside the tube and samples were drawn from time to time weighed and analysed (titration of tin(II) with iodine), see Figure A-1.

The second series of measurements seems to be more reliable. Equilibration time is unknown and may be in the range of minutes. The author states that the results are not of high accuracy.

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<sup>1</sup> The mathematical symbol  $\hat{=}$  means corresponds to, see [2007COH/CVI].

Figure A-1: Solubility of  $\text{SnI}_2(\text{s})$  in water at different temperatures ( $\square$ : first series of measurements;  $\circ$ : second series of measurements; solid line: fit of first series).



### [1899COH]

Although below 20 °C the grey ( $\alpha$ ) modification of tin is the stable one, yet the white ( $\beta$ ) modification may be supercooled, and an element may accordingly be constructed of the form: Electrode of grey tin | Solution of a tin salt | Electrode of white tin. The cell potential will be  $E = (RT/zF) \log_{10}(P_g/P_w)$  for this element where  $z$  is the valency of the tin,  $P_g$  and  $P_w$  the electrolytic solution pressures of the grey and white modifications respectively. Actual measurement of the cell potential showed that the ratio  $P_g/P_w$  was 1 at 20 °C, the transition temperature, and  $> 1$  at temperatures below 20 °C. Thus the white ( $\beta$ ) modification has the greater electrolytic solution pressure, and will precipitate grey ( $\alpha$ ) tin from solutions of tin salts below 20 °C, a conclusion confirmed by experiment. This explains why a solution of a tin salt is highly favourable to the conversion of the white into the grey modification. When  $E_1$  is the difference of potential between the grey tin and the tin solution in which it is immersed,  $H_1$  the heat of ionisation of the grey tin, and  $F$  is the Faraday constant, then  $E_1 = H_1/zF + T dE_1/dT$ : a corresponding relation holds for the other electrode. Combining these with Clapeyron's equation  $T \cdot dp^{\alpha+\beta}/dT = \Delta_\alpha^\beta H_m^* / \Delta_\alpha^\beta V_m^*$ , where  $p^{\alpha+\beta}$  is the external pressure,  $\Delta_\alpha^\beta H_m^*$  the heat absorbed when 1 mol of grey tin is converted into white tin, and  $\Delta_\alpha^\beta V_m^*$  is the molar volume difference of white and grey modifications, the author deduces the equation  $dT/dp^{\alpha+\beta} = \Delta_\alpha^\beta V_m^* / zF(dE_1/dT - dE_2/dT)$ .

**[1899COH/EIJ]**

## Summary of results

1. The disintegration of the white tin into gray tin, first described in 1851, is a reversible phase transformation.
2. The transition temperature,  $T_{\text{trs}} = 293$  K, has been determined by dilatometry and using the electrochemical cell Sn(white) | Sn-salt | Sn(grey).
3. A transition temperature of 20 °C means that, apart from warm days, our whole “tin world” is metastable.
4. The rate of phase transformation Sn(white)  $\rightarrow$  Sn(grey) has been determined and has a maximum at 225 K.
5. Contact of white tin with an aqueous  $(\text{NH}_4)_2\text{SnCl}_6$  solution or with grey tin or simultaneous contact with  $(\text{NH}_4)_2\text{SnCl}_6$  solution and grey tin accelerates the phase transformation. In this way it is easy to prepare any quantity of grey tin.

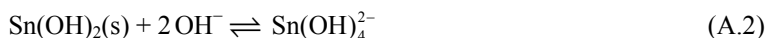
**[1902RUB]**

Tin(II) hydroxide was precipitated from freshly prepared tin(II) chloride solutions by adding sodium hydroxide. The precipitate was washed and surplus water was squeezed out. Then the precipitate was equilibrated with carbon dioxide free sodium hydroxide solutions in the concentration range  $0.5 < c_{\text{NaOH}}/\text{mol}\cdot\text{dm}^{-3} < 4.7$ . During this procedure black-blue crystals of tin(II) oxide were formed. Saturated solutions were obtained after reaction periods of 5h. The tin content of the saturated solutions was transformed to  $\text{SnO}_2(\text{s})$  and determined gravimetrically. Equilibration was certainly carried out under ambient conditions, but no precise value of temperature was reported. No attempt was made to characterise “ $\text{Sn}(\text{OH})_2(\text{s})$ ” stoichiometrically and/or structurally. In Table A-1 Rubenbauer’s original data are listed in columns 1 and 2 and converted into concentrations in columns 3, 4 and 5.

Table A-1: Solubility of “ $\text{Sn}(\text{OH})_2(\text{s})$ ” in NaOH solutions.

$\rho_{\text{Na}}/\text{g}\cdot\text{cm}^{-3}$	$\rho_{\text{Sn}}/\text{g}\cdot\text{cm}^{-3}$	$[\text{NaOH}]_{\text{tot}}/\text{mol}\cdot\text{dm}^{-3}$	$[\text{OH}^-]_{\text{free}}/\text{mol}\cdot\text{dm}^{-3}$	$[\text{Sn}(\text{II})]_{\text{tot}}/\text{mol}\cdot\text{dm}^{-3}$
0.012400	0.009520	0.53937	0.45917	0.08020
0.018400	0.013070	0.80036	0.69026	0.11010
0.031970	0.021520	1.39062	1.20934	0.18128
0.041630	0.027800	1.81081	1.57662	0.23418
0.048305	0.039245	2.10115	1.77056	0.33060
0.106170	0.094670	4.61814	3.82065	0.79749

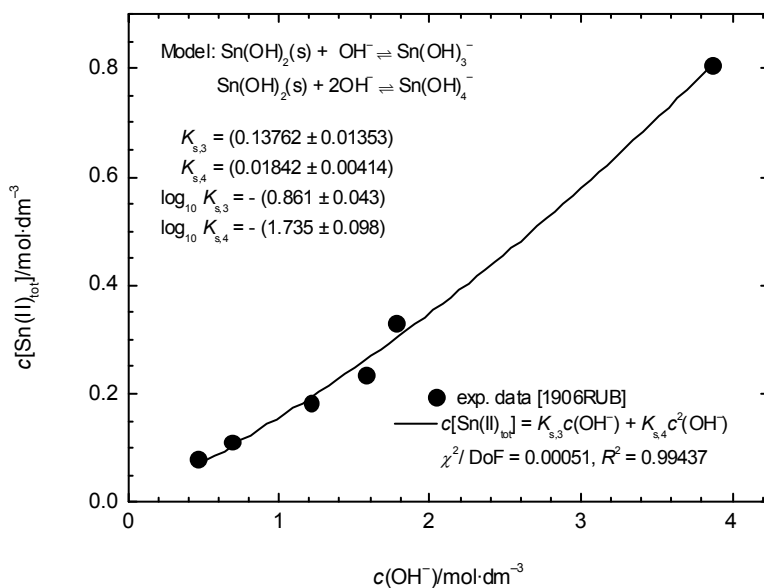
A plot of  $[\text{Sn(II)}]_{\text{tot}}$  vs.  $[\text{OH}^-]_{\text{free}}$  can be interpreted by the following equilibria leading to Eq. (A.3), see also Figure A-2:



$$[\text{Sn(II)}]_{\text{tot}} = K_{s,3} [\text{OH}^-] + K_{s,4} [\text{OH}^-]^2 \quad (\text{A.3})$$

where  $\log_{10} K_{s,3} = -(0.86 \pm 0.04)$  and  $\log_{10} (K_{s,4}/\text{dm}^3 \cdot \text{mol}^{-1}) = -(1.73 \pm 0.10)$ .

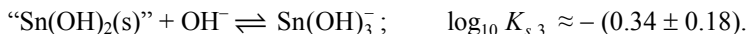
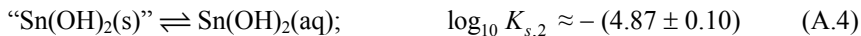
Figure A-2: Solubility of “ $\text{Sn(OH)}_2(\text{s})$ ” in NaOH solutions.



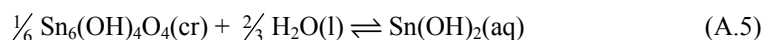
Although the methodology of [1902RUB] has deficiencies  $\log_{10} K_{s,3}$  agrees within the experimental uncertainty with the value derived from Garret and Heiks' work [1941GAR/HEI]. In addition [1902RUB] indicates formation of  $\text{Sn(OH)}_4^{2-}$  or  $\text{SnO(OH)}_2^{2-}$ , a species not mentioned by previous reviews on tin species [1976BAE/MES], [2001SEB/POT], [2002HUM/BER].

### [1906GOL/ECK]

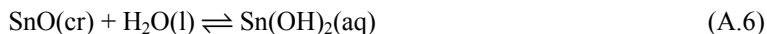
In this work the reduction of nitroanilines, nitrophenols, nitrobenzoic acids, nitrobenzenesulfonic acids, and nitrobenzaldehydes was investigated. In the introductory part the solubility of “tin hydroxide” in  $\text{H}_2\text{O}$  and dilute solutions of NaOH was also described. The experimental data were explained by two equilibria:



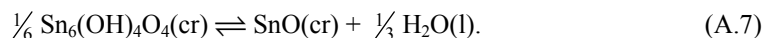
The compound “Sn(OH)<sub>2</sub>(s)” was precipitated from SnCl<sub>2</sub> solutions with NaOH. The equilibrium constant,  $K_{s,2}$ , of Reaction (A.4) was determined by equilibrating precipitated “Sn(OH)<sub>2</sub>(s)” with H<sub>2</sub>O. The equilibrium concentration of Sn(II) was determined by iodometric titration. No attempt was made to characterise “Sn(OH)<sub>2</sub>(s)” stoichiometrically and/or structurally. Consequently it is not quite justified to ascribe the value  $\log_{10} K_{s,2}((\text{A.5}), 298.15 \text{ K}) = -4.87$  to hexatin tetrahydroxide tetroxide, Sn<sub>6</sub>(OH)<sub>4</sub>O<sub>4</sub>, as in Reaction (A.5), but lacking any thermodynamic information on the latter phase it is suggested we do so.



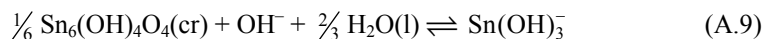
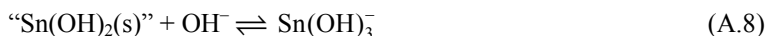
Garret and Heiks [1941GAR/HEI] reported  $\log_{10} K_{s,2}((\text{A.6}), 298.15 \text{ K}) = - (5.30 \pm 0.13)$  for Reaction (A.6) which differs by 0.43 log<sub>10</sub> units from  $\log_{10} K_{s,2}((\text{A.5}), 298.15 \text{ K})$  although it was obtained by a similar method.



It is again not quite justified to ascribe this difference to Reaction (A.7), but  $\Delta_r G_m^{\circ}((\text{A.7}), 298.15 \text{ K}) = - (2.45 \pm 1.05) \text{ kJ}\cdot\text{mol}^{-1}$  is at least qualitatively in line with the observation that white “Sn(OH)<sub>2</sub>(s)” transforms spontaneously into blue-black SnO(cr)



For Reaction (A.8) or (A.9)



leading to  ${}^*K_{s,3}$  the sum of the stoichiometric coefficients of the participating ionic species vanishes,  $\sum \nu_B = 0$ , see Eq. (II.38).

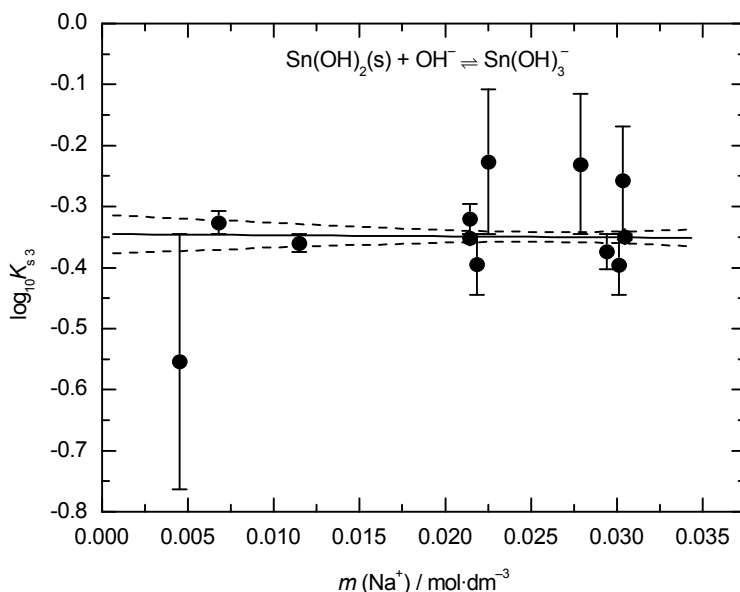
Thus  ${}^*K_{s,3}$  does not need to be converted when the composition scale is changed from molarity to molality. Moreover,  $\Delta z^2 = 0$  for Reactions (A.8) and (A.9) and thus the Debye-Hückel term vanishes and likewise in the course of ionic strength corrections. In Figure A-3  $\log_{10} {}^*K_{s,3}(\text{A.9})$  is plotted vs.  $m_{\text{Na}^+}$ . The range of sodium ion concentrations covered by the experiments is too narrow to allow a reliable estimation of  $\Delta \epsilon$ .

The mean value of  $\log_{10} {}^*K_{s,3}^{\circ}(\text{A.9})$  is  $(0.50 \pm 0.18)$  log<sub>10</sub> units higher than  $\log_{10} {}^*K_{s,3}^{\circ}$  evaluated from [1941GAR/HEI] which refers to SnO(cr). This leads to  $\Delta_r G_m^{\circ}((\text{A.7}), 298.15 \text{ K}) = - (2.85 \pm 1.03) \text{ kJ}\cdot\text{mol}^{-1}$  which agrees surprisingly with the value  $- (2.45 \pm 0.91) \text{ kJ}\cdot\text{mol}^{-1}$  derived from comparison of  $\log_{10} K_{s,2}$  values for Reactions (A.5) and (A.6), although in the experiments of [1906GOL/ECK] an



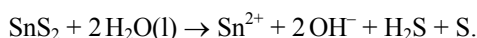
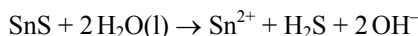
unknown amount of chloride ions may have contributed to the solubility of “Sn(OH)<sub>2</sub>” or Sn<sub>6</sub>(OH)<sub>4</sub>O<sub>4</sub>(cr).

Figure A-3:  $\log_{10} K_{s,3}$  (A.9) vs.  $m_{\text{Na}^+}$  (●: experimental; solid line: linear regression ( $\log_{10} K_{s,3} = -(0.34 \pm 0.18)$ ); dashed lines: confidence limits).



### [1906WEI]

Solubility of a series of sulfides was determined in water at  $(18 \pm 0.03)^\circ\text{C}$ . Solute concentration was calculated from electrical conductivities using the values for ion mobilities. Conductivity of pure water was less than  $1.5 \times 10^{-6}$ . The calculations were based on the following hydrolytic reactions:



The following ion mobility values had been used (no units given):  $\text{OH}^- = 174$ ;  $0.5 \text{Sn}^{2+} = 61.5$ . The conductivity contribution of dissolved  $\text{H}_2\text{S}$  was neglected. Separate conductivity measurements of  $\text{H}_2\text{S}$  solutions gave support for this approximation.

SnS was prepared by heating of precipitated tin sulfide to 1273 K in a stream of pure nitrogen. Chemical analysis of black well crystallised product showed an excess of tin of about 1 mass-%. For SnS<sub>2</sub> a sample of “Musivgold” from Schuchardt was used.

The author obviously worked carefully and compared several of his own sulfide solubility data with data from other references and found excellent agreement for  $Tl_2S$ , however, the method of concentration determination is not easy to check.

The data for tin sulfides are:

$SnS_2$ , Musivgold	$1.13 \times 10^{-6}$ M after 24 h rotation
$SnS$ , crystallised	$0.14 \times 10^{-6}$ M after 7 h rotation.

### [1907WEI]

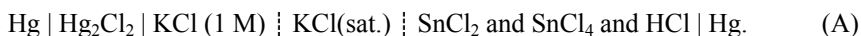
The article represents an extract from a detailed paper in [1906WEI]. Solubility of a series of sulfides was determined in water at  $(18 \pm 0.03)^\circ C$ . Solute concentration was calculated from electrical conductivity using values for ion mobility. The author assumed that the conductivity of  $H_2S$  solutions were measured separately. The same data as in [1906WEI] are reported.

### [1914BRO]

The heat evolution accompanying the transformation,  $Sn(\text{white}) \rightarrow Sn(\text{grey})$ , has at 273 K the value  $\Delta_{\text{white}}^{\text{gray}} H_m^* = -2.23 \text{ kJ} \cdot \text{mol}^{-1}$ . The heat capacity of both modifications of Sn has been measured at a number of temperatures between 80 and 273 K. The values obtained agree with values previously determined at  $283^\circ$ . It has been found that the course of the  $H$  and  $G$  curves agrees with Nernst's theorem.

### [1914FOR/BAR]

The potentials of aqueous mixtures of  $SnCl_2$  and  $SnCl_4$  containing 0.25 and  $0.125 \text{ mol} \cdot \text{dm}^{-3}$  Sn in HCl of three concentrations were measured at Hg electrodes at  $25^\circ C$  using the following cell



The probable error was estimated to be  $\pm 2$  mV. Hg is preferable to Pt in the measurement of oxidising potentials of low intensity. Results are more quickly obtained and suffer less from irregularities in surface energy of the electrode and the presence of traces of  $O_2$ . Reducing the total Sn concentration from 0.25 to  $0.125 \text{ mol} \cdot \text{dm}^{-3}$  makes the potential slightly more electronegative; but this effect hardly exceeds the experimental uncertainty. By extrapolation to zero concentration of acid, results were obtained which should be largely unaffected by uncertainties due to hydrolysis and to the potential at the liquid junction. Up to  $2 \text{ mol} \cdot \text{dm}^{-3}$  HCl the potentials measured with cell (A) are, according to the authors, quite accurately expressed by Eq. (A.10)

$$\pi/V = 0.426 + 0.030 \log_{10} \{ [Sn(IV)]/[Sn(II)] \} - 0.011 [HCl] \quad (A.10)$$

provided sufficient acid is added to check hydrolysis. With the measured electrode potentials referring to the standard hydrogen electrode  $E(Sn(IV)/Sn(II)) = \pi -$

$E'$  (calomel 1 M KCl) Eq. (A.10) had to be modified in order to conform with NEA TDB conventions

$$E/V = E^{\circ}/V + 0.030 \cdot \log_{10} \{[\text{Sn(IV)}]/[\text{Sn(II)}]\} - 0.011 [\text{HCl}]. \quad (\text{A.11})$$

The composition of solutions at the instant of potential measurement was calculated from the initial concentrations  $c^{\circ}(\text{Sn}(\beta))$ ,  $c^{\circ}(\text{HCl})$  and the actual ratio  $[\text{Sn(IV)}]/[\text{Sn(II)}]$  determined by the authors analytically. For conversion of  $\pi$  to  $E$  according to the relationship mentioned above  $E'$  (calomel 1 M KCl) = 280.1 mV was taken from [1961IVE/JAN] (pg. 161).

Forbes and Bartlett assume that  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+})$  can be estimated according to a semi-empirical approach  $E - (RT \cdot \ln(10))/2F \cdot \log_{10} \{c_{\text{Sn(IV)}}/c_{\text{Sn(II)}}\} \approx E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}) + \text{const} \cdot c_{(\text{Cl})\text{tot}}$ , because Sn(IV) as well as Sn(II) chlorido complexes become negligible when  $c_{(\text{Cl})\text{tot}}$  goes to zero. Thus the left-hand side of this equation has been plotted vs.  $c_{(\text{Cl})\text{tot}}$ , see Figure A-4.

Linear regression of the data given by [1914FOR/BAR] and results in

$$E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}, 298.15 \text{ K}) = (145.1 \pm 1.8) \text{ mV}$$

and

$$b = -(9.4 \pm 0.7) \text{ mV} \cdot \text{mol}^{-1} \cdot \text{dm}^3.$$

While the agreement between original and recalculated values is quite good, the result is flawed by systematic errors from two sources.

1) Although Sn(II) as well as Sn(IV) chlorido complexes vanish as  $m_{(\text{Cl}^-)\text{tot}}$  goes to zero, they do so in a highly non-linear way.

$$m_{\text{Sn}^{4+}}/m_{\text{Sn}^{2+}} = \{m_{\text{Sn(IV)}}/m_{\text{Sn(II)}}\} \cdot \{(1 + \beta_{1(2)} m_{\text{Cl}^-} + \dots)/(1 + \beta_{1(4)} m_{\text{Cl}^-} + \beta_{2(4)} m_{\text{Cl}^-}^2 \dots)\} \quad (\text{A.12})$$

$$E - (RT \ln(10))/2F \cdot \log_{10} \{m_{\text{Sn}^{4+}}/m_{\text{Sn}^{2+}}\} = E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}) \quad (\text{A.13})$$

$$E - (RT \ln(10))/2F \cdot \log_{10} \{m_{\text{Sn(IV)}}/m_{\text{Sn(II)}}\} = E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}) + (RT \ln(10))/2F \cdot \log_{10} \{(1 + \beta_{1(2)} m_{\text{Cl}^-} + \dots)/(1 + \beta_{1(4)} m_{\text{Cl}^-} + \beta_{2(4)} m_{\text{Cl}^-}^2 \dots)\} \quad (\text{A.14})$$

This problem is schematically depicted in Figure A-5.

2) At least in the lower part of the pertinent acidity range,  $0.5 \leq m_{\text{HCl}} \leq 5.4 \text{ mol} \cdot \text{kg}^{-1}$ , Sn(IV) hydroxido complexes are doubtlessly stable. Thus there was no chance to estimate  $m_{\text{Sn}^{4+}}$  correctly and the attempted SIT analysis resulted in a too low value of  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+})$ .

Figure A-4:  $E_{\text{app,HCl}}^{\circ}$  of Sn(IV)/Sn(II) vs.  $c_{\text{Cl}^-}^{\text{tot}}$  (experimental data of [1914FOR/BAR] (●), solid line, ★:  $E_{\text{app},0}^{\circ} = (145.1 \pm 1.8) \text{ mV}$ ).

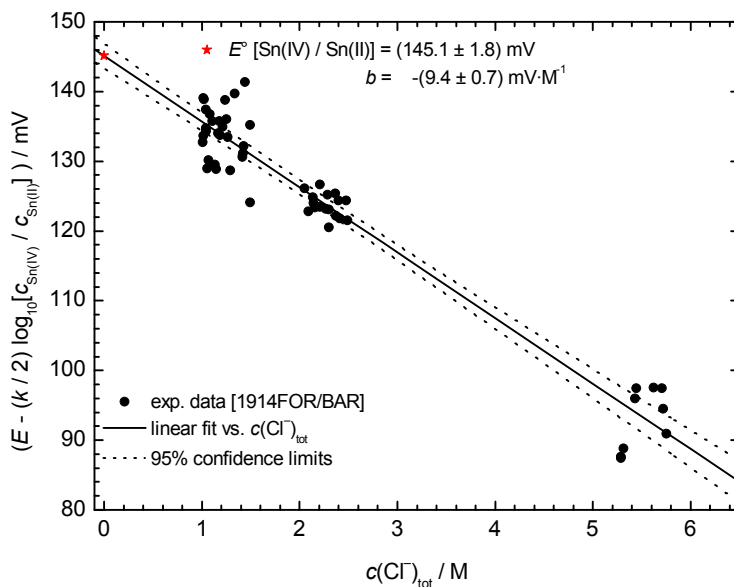
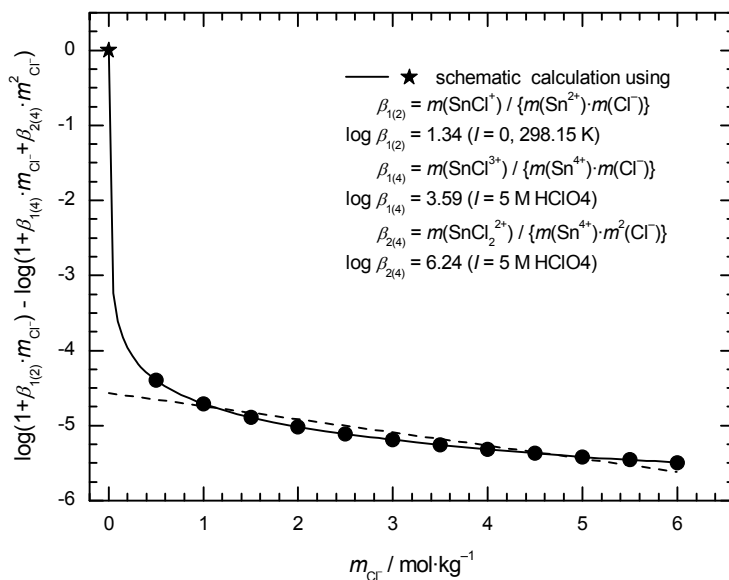


Figure A-5: Correction term connecting  $\log_{10} \{m_{\text{Sn(IV)}}/m_{\text{Sn(II)}}\}$  and  $\log_{10} \{m_{\text{Sn}^{4+}}/m_{\text{Sn}^{2+}}\}$  depends on  $m_{\text{Cl}^-}$  (●: actual measurements; ★: (0,0) schematic calculation using  $\beta_{1(2)} = m_{\text{SnCl}^+} / \{m_{\text{Sn}^{2+}} \cdot m_{\text{Cl}^-}\}$ ; dashed line: linear extrapolation of the data).



**[1917KEL]**

Minute brilliant crystals were observed in a cavity inside a metallic mass found in an Indian cemetery on Hogtown Bayou, Santa Rosa County, Florida. The metal was recognised as tin. The crystals were dissolved by being boiled with aqueous sodium carbonate solution. Tin and chlorine were determined gravimetrically as SnO<sub>2</sub>(s) and AgCl(s), respectively.

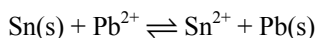
The analytical results (see Table A-2) are consistent with the empirical formula SnCl<sub>2</sub>·SnO. The presence of abhurite in these crystals, found on metallic tin in an Indian mound, seems to be obvious, but without being confirmed by an X-ray investigation it remains rather speculative.

Table A-2: Composition of tin(II) oxide hydroxide chloride [1917KEL].

Composition	Exp. 1 corr.	Exp. 2	SnCl <sub>2</sub> ·SnO	Sn <sub>21</sub> Cl <sub>16</sub> (OH) <sub>14</sub> O <sub>6</sub> (cr) abhurite
w(Sn)	71.10%	73.06%	73.20%	73.45%
w(Cl)	21.74%	21.98%	21.68%	16.71%
w(diff.)	7.16%	4.96%	4.93%	9.84%

**[1917NOY/TOA]**

The equilibrium constant of the following reaction



was determined in aqueous HClO<sub>4</sub>-Sn(ClO<sub>4</sub>)<sub>2</sub>-Pb(ClO<sub>4</sub>)<sub>2</sub> solutions at 25 °C. Equilibrium was attained from both sides within 10 to 19 days. The mean values of 11 independent measurements given were  $m_{\text{Sn}^{2+}}/m_{\text{Pb}^{2+}} = (2.98 \pm 0.02)$ ,  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Pb}^{2+}/\text{Pb}(0)) = -(RT \ln(10)/2F) \cdot \log_{10} [m_{\text{Sn}^{2+}}/m_{\text{Pb}^{2+}}] = -(14.0 \pm 0.1)$  mV.

The re-evaluation of these experimental data neglecting the ionic strength dependence resulted in

$$E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Pb}^{2+}/\text{Pb}(0)) = -(14.03 \pm 0.29)$$
 mV.

When  $(RT \ln(10)/2F) \cdot \log_{10} ([\text{Sn}^{2+}]/[\text{Pb}^{2+}])$  is plotted vs.  $m_{\text{ClO}_4^-}$  (see Figure A-6) the slope of the linear regression line is  $-(RT \ln(10)/2F) \cdot \Delta \epsilon$ , where  $\Delta \epsilon = \epsilon(\text{Sn}^{2+}, \text{ClO}_4^-) - \epsilon(\text{Pb}^{2+}, \text{ClO}_4^-)$ .

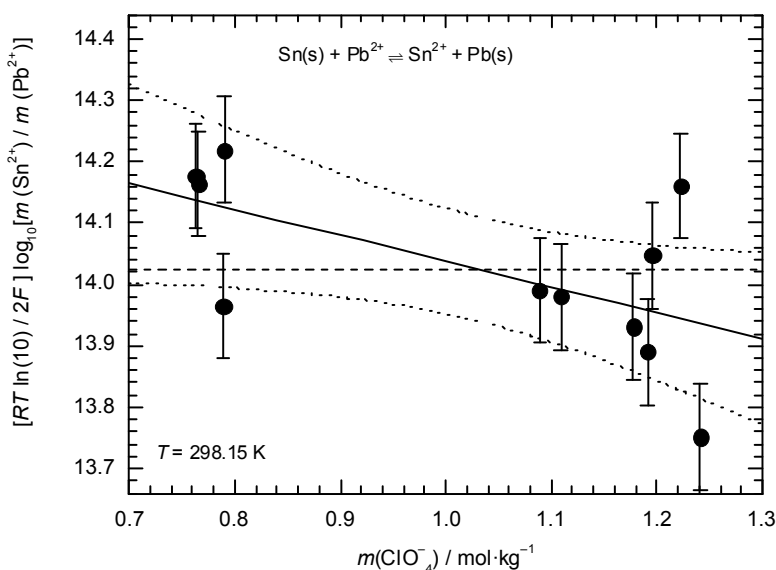
The value of the difference of the standard potentials extrapolated to  $m_{\text{ClO}_4^-} = 0$  is

$$E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Pb}^{2+}/\text{Pb}(0)) = -(14.46 \pm 0.31)$$
 mV.

As  $m_{\text{ClO}_4^-}$  is varying from 0.76 to 1.24 mol·kg<sup>-1</sup> only, the reliability of  $\Delta \epsilon$  thus obtained, should not be overestimated. Consequently the value of  $\epsilon(\text{Sn}^{2+}, \text{ClO}_4^-) =$

0.164 kg·mol<sup>-1</sup> predicted by these data was not selected in this review.

Figure A-6: Variation of  $(RT \ln(10)/2F) \cdot \log_{10} [m_{\text{Sn}^{2+}}/m_{\text{Pb}^{2+}}]$  vs.  $m_{\text{ClO}_4^-}$  (●: experimental data; error bars ( $\pm 0.086$  mV) comply with the uncertainty of  $[m_{\text{Sn}^{2+}}/m_{\text{Pb}^{2+}}]$  given by [1917NOY/TOA]; solid line: linear fit; dotted lines: 95% confidence limits; dashed line: mean value of  $(E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Pb}^{2+}/\text{Pb}(0)))$  neglecting the ionic strength dependence).



### [1919CAR]

It was attempted to determine the composition of the precipitates formed when tin(II) chloride was decomposed by water. Baker & Adamson's C. P.  $\text{SnCl}_2$  was treated with metallic tin and hydrochloric acid; the mixture was boiled gently until most of the free acid was removed and was then allowed to cool down. The crystals which deposited were drained as thoroughly as possible and dried between filter papers. These crystals were boiled with water, the precipitate was filtered off, the mother liquors were preserved and allowed to cool down overnight to 25 °C. In one case crystals forming hexagonal rosetts were obtained. Analysis of this material gave 73.63% Sn and 16.51% Cl, and the formula  $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$  was ascribed to it. Precipitates of this composition, but less well crystallised, are commonly formed by the action of potassium hydroxide on an excess of tin(II) chloride.

Only Sn and Cl contents of the crystalline material were determined. In Table A-3 the stoichiometrically required composition is given in parentheses. The analytical results of the hexagonal rosetts agree at least as good with  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  as with  $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$ . Thus Carson probably synthesised the same tin(II) hydroxide chloride phase as did von Schnering *et al.* [1981SCH/NES] who definitively described its structure. Carson believed that a compound  $2\text{SnCl}_2 \cdot 7\text{Sn}(\text{OH})_2$  had been prepared, which is the most basic tin(II) chloride. The analytical results agree approximately with  $2\text{SnCl}_2 \cdot 7\text{SnO}$ , but not with  $2\text{SnCl}_2 \cdot 7\text{Sn}(\text{OH})_2$ , as Table A-3. The “most basic tin(II) chloride” is rather a mixture than a compound.

Table A-3: Composition of tin(II) chloride hydroxide oxide [1919CAR].

Composition	$3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}(\text{s})$ hexagonal rosetts	$2\text{SnCl}_2 \cdot 7\text{Sn}(\text{OH})_2$ “most basic salt”	$\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ abhurite
w(Sn)	73.63 (73.25)%	80.10 (73.77)%	73.45%
w(Cl)	16.51 (16.41)%	10.58 (9.79)%	16.71%
w(O)	(9.87)%	-	9.43%
w(H)	(0.47)%	-	0.42%
w(O) + w(H)	9.86 (10.34)%	9.32 (16.44)%	9.85%

**[1922BUR/PAR]**

Tin(II) hydroxides were prepared by methods described by [1844SCH], [1882DIT2] and other authors. Analyses were carried out on tin(II) hydroxide samples synthesised by five different methods. These samples had essentially the same composition favouring the formula  $3\text{SnO} \cdot 2\text{H}_2\text{O}$ .

**[1925BRI2]**

Tin(II) chloride solutions were titrated with sodium hydroxide and the precipitation was studied using the hydrogen electrode. The composition varied from  $\text{SnCl}_{1.33}(\text{OH})_{0.67}$  at  $\text{pH} \approx 1.9$  to  $\text{Sn}_{0.14}(\text{OH})_{1.86}$  at  $\text{pH} \approx 7$ .

Tin(II) hydroxides are treated in a comparatively short subsection on pg. 2132 and 2133. No quantitative information *e.g.* concerning its solubilities is given.

**[1925SMR]**

This investigation of the electrodeposition of tin was undertaken to complete the table of deposition potentials of metals at the dropping mercury cathode and to examine the basic and acidic properties of “tin hydroxide”.



**[1926CAR]**

Tin(II) sulfate was dissolved in water, heated to 100 °C and sodium hydroxide solutions were added. White precipitates formed which, within two regions of alkali concentrations, remained nearly constant in composition. The formulae  $\text{SnSO}_4 \cdot \text{SnO}$  and  $\text{SnSO}_4 \cdot 2\text{SnO} \cdot \text{H}_2\text{O}$  were assigned to these compounds.

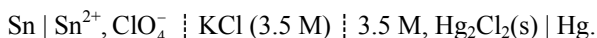
The analytical method used is rather insensitive to the  $\text{H}_2\text{O}$  content of the synthesised basic tin(II) sulfates. Thus it is by no means sure that anhydrous  $\text{SnSO}_4 \cdot \text{SnO}$  has been indeed prepared.

**[1927LEW/RAN]**

The German version of the classical textbook of Chemical Thermodynamics was consulted because Haring and White [1938HAR/WHI] used the “independent ionic activity coefficients” listed in this book.

**[1928PRY]**

The standard potential for  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \beta\text{-Sn}$  was determined at 24.5 °C in aqueous perchlorate solutions using the cell

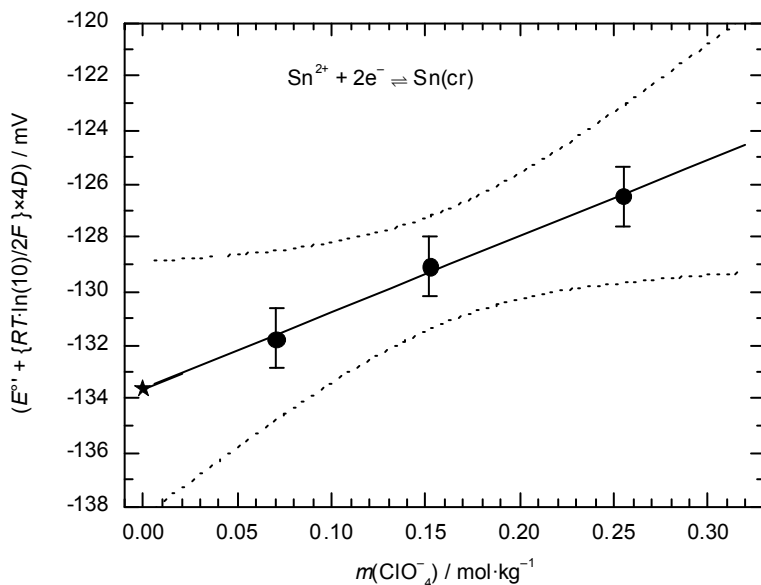


Potentiometric measurements were carried out on 0.01 M  $\text{SnCl}_2$  and 0.01 M  $\text{SnBr}_2$  solutions with increasing chloride and bromide concentrations, respectively.

The standard potential data for  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \beta\text{-Sn}$  determined by Prytz were used by [1999LOT/OCH] and [2002HUM/BER] for their critical evaluation. Direct potentiometric measurements of this standard potential are rather scarce and consequently extremely valuable. The original mean value of  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 297.65 \text{ K}) = -(135.6 \pm 0.6) \text{ mV}$  deviates by 7.4 mV from the value recommended by CODATA [1989COX/WAG]  $(-143.0 \pm 2.1) \text{ mV}$ . In the course of the re-evaluation of these data the potential of the 3.5 M calomel electrode vs. SHE at 24.5 °C must be taken into account. Ives and Janz [1961IVE/JAN] list values for this potential from 40 to 90 °C. For extrapolation to 24.5 °C a function  $E^\circ = A + B T + C T \cdot \ln T$  was fitted to the  $E^\circ, T$  pairs given. This led to the following extrapolated value  $E^\circ(3.5 \text{ M KCl, calomel, } 24.5 \text{ }^\circ\text{C}) = (253.7 \pm 1.0) \text{ mV}$ , which differs by 3.2 mV from the value taken from directly measured, unpublished data of A. Unmack [1928PRY]. As this deviation exceeds the expected experimental error considerably, the value used by Prytz,  $E^\circ(3.5 \text{ M KCl, calomel, } 24.5 \text{ }^\circ\text{C}) = (250.5 \pm 1.0) \text{ mV}$ , was accepted for the SIT recalculation. Finally a value of  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 297.65 \text{ K}) = -(133.6 \pm 1.5) \text{ mV}$  was obtained, (see Figure A-7). For comparison with  $E^\circ$  values determined at 298.15 K a minor correction was applied, based on  $S_m^\circ(\text{Sn}^{2+})$  selected in this review, which resulted in  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 298.15 \text{ K}) = -(133.54 \pm 3.00) \text{ mV}$  and  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(25.77 \pm 0.58) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.



Figure A-7: Variation of  $\{E^{\circ} + 4D RT \ln(10)/2F\}/\text{mV}$  vs.  $m_{\text{ClO}_4^-}$  (●: Experimental data at 24.5 °C; error bars ( $\pm 0.1$  mV) comply with the uncertainty of  $E^{\circ}$  values given by [1928PRY]; ★:  $E^{\circ}(\text{Sn}^{2+}/\text{Sn}(0))$ ; solid line: linear fit; dotted lines: 95% confidence limits).



The value of  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-)$  derived from these data was not reliable enough for use in this review.

The stepwise formation constants of the mononuclear complexes  $\text{SnX}_q^{2-q}$  were determined, with  $q = 1, 2, 3, 4$  for  $X = \text{Cl}$  and  $q = 1, 2, 3$  for  $X = \text{Br}$ .

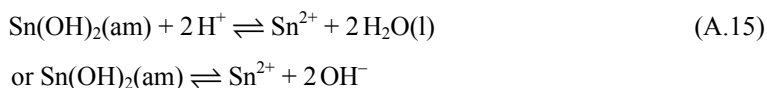
The reported thermodynamic formation constants for the tin(II)-chlorido and -bromido complexes were derived using the Debye-Hückel equation, which is not compatible with the SIT. Therefore, the experimental data were re-evaluated using the SIT approach for the purposes of this review. However, several complications arose during the recalculation: (i) the author used a mixture of electrolytes to increase the chloride (HCl and KCl) or bromide (HBr and KBr) concentrations, (ii) only a few experimental data points are available, which do not allow the parallel refinement of all the parameters ( $\beta_1, \beta_2, \beta_3, \varepsilon(1), \varepsilon(2), \varepsilon(3)$  and  $\varepsilon(\text{Sn}^{2+}, X^-)$ ) required for a correct SIT treatment. A “manually controlled” refinement revealed that the formation of three complexes ( $\text{SnX}^+, \text{SnX}_2(\text{aq}), \text{SnX}_3^-$ , where  $X = \text{Cl}^-$  or  $\text{Br}^-$ ) is sufficient to account for the observed potential changes. For the chlorido complexes the following parameters were obtained:  $\log_{10} \beta_1^{\circ} = 1.34$  ( $\Delta\varepsilon(\text{KCl}) = -0.10 \text{ kg} \cdot \text{mol}^{-1}$ ),  $\log_{10} \beta_2^{\circ} = 2.13$

( $\Delta\varepsilon(\text{KCl}) = -0.14 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_3^0 = 1.99$  ( $\Delta\varepsilon(\text{KCl}) = -0.19 \text{ kg}\cdot\text{mol}^{-1}$ ) and  $\varepsilon(\text{Sn}^{2+}, \text{Cl}^-) = 0.14 \text{ kg}\cdot\text{mol}^{-1}$ . The analogue values of the bromido complexes are as follows:  $\log_{10} \beta_1^0 = 0.92$  ( $\Delta\varepsilon(\text{KBr}) = 0.06 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_2^0 = 1.53$  ( $\Delta\varepsilon(\text{KBr}) = -0.13 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_3^0 = 1.47$  ( $\Delta\varepsilon(\text{KBr}) = -0.18 \text{ kg}\cdot\text{mol}^{-1}$ ) and  $\varepsilon(\text{Sn}^{2+}, \text{Br}^-) = 0.12 \text{ kg}\cdot\text{mol}^{-1}$ . Considering the mentioned difficulties an uncertainty of  $\pm 0.10$  has been assigned to  $\varepsilon(\text{Sn}^{2+}, \text{Cl}^-)$  and  $\varepsilon(\text{Sn}^{2+}, \text{Br}^-)$  and an uncertainty of  $\pm 0.5$  has been assigned to the above  $\log_{10} \beta_q^0$  values.

### [1928PRY2]

Potentiometric titrations of acidic Sn(II) chloride, bromide and perchlorate solutions with sodium hydroxide solutions were carried out. After the excess acid had been neutralised a white precipitate, supposedly tin(II) hydroxide, came down. The precipitate was not characterised with respect to its composition and structure, it was assumed to be amorphous Sn(OH)<sub>2</sub>. Prytz estimated for the solubility product of Sn(OH)<sub>2</sub>:  $\log_{10} K_{s,0} \approx -25.3$ .

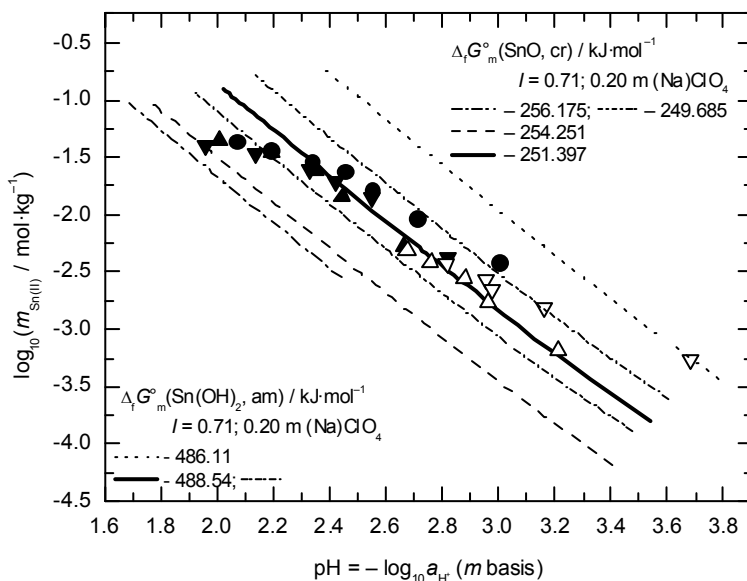
In perchlorate solutions the solubility of (amorphous?) tin(II) hydroxide will be determined by Reaction (A.15),



whereas in chloride and bromide solutions a considerable fraction of dissolved tin(II) will consist of the respective halogeno complexes. Usually solubility data provide reliable information for the predominating species only. Thus the experiments in perchlorate media were digitalised and recalculated. The pH values reported by Prytz were considered to represent  $-\log_{10} a_{\text{H}^+}$ , where  $a_{\text{H}^+}$  is the activity of hydrogen ions on the molar scale. The equilibrium concentration of Sn(II) was estimated using the analytical data and assuming that each mole of OH<sup>-</sup> in excess precipitates 0.5 mole of Sn(OH)<sub>2</sub>(am).

The equilibrium concentration (or molality) of tin(II) depends on pH and to a lesser degree on ionic strength, see Figure A-8. A cautious estimation results in  $\log_{10} {}^*K_{s,0}(\text{A.15}) = (2.38 \pm 0.50)$ , which is almost the same value [2002HUM/BER] arrived at for Sn(OH)<sub>2</sub>(precip.).

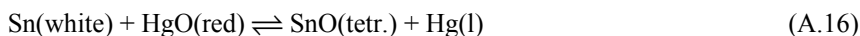
Figure A-8: Equilibrium concentration of  $\text{Sn}^{2+}$  as a function of pH (experimental data:  $\blacktriangle$ :  $I = 0.220 \text{ M}$ ,  $\blacktriangledown$ :  $I = 0.190 \text{ M}$ ,  $\triangle$ :  $I = 0.025 \text{ M}$ ,  $\nabla$ :  $I = 0.020 \text{ M}$ ,  $\bullet$ :  $I = 0.710 \text{ m}$ ).



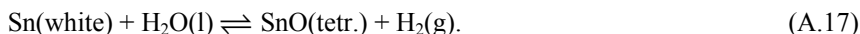
### [1929MAI]

Oxide electrodes of cadmium oxide, cuprous and cupric oxide, Sn(II) and Sn(IV) oxide and lead dioxide have been compared to the hydrogen or mercuric electrode in barium hydroxide solutions. For the determination of  $\Delta_f G_m^\circ(\text{SnO, tetr.}, 298.15 \text{ K})$  two galvanic cells were employed:

1. Hg | HgO electrode:  $\text{Sn(white)} | \text{SnO(tetr.)} | \text{Ba(OH)}_2(\text{aq}) | \text{HgO(red)} | \text{Hg(l)}$



2. Hydrogen electrode:  $\text{Sn(white)} | \text{SnO(tetr.)} | \text{Ba(OH)}_2(\text{aq}) | \text{H}_2(\text{g}) | \text{Pt}$



Accepting  $S_m^\circ(\text{SnO, tetr.}, 298.15 \text{ K}) = 56.74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [1929MIL2], Maier arrived at

$$\Delta_f G_m^\circ(\text{SnO, tetr.}, 298.15 \text{ K}) = -(256.61 \pm 1.26) \text{ kJ}\cdot\text{mol}^{-1} \text{ and}$$

$$\Delta_f H_m^\circ(\text{SnO, tetr.}, 298.15 \text{ K}) = -(284.15 \pm 1.26) \text{ kJ}\cdot\text{mol}^{-1}.$$

The cell potential values of Table VI [1929MAI] were recalculated using  $\Delta_f G_m^\circ(\text{HgO, red}, 298.15 \text{ K}) = -(58.540 \pm 0.050) \text{ kJ}\cdot\text{mol}^{-1}$  [1989COX/WAG], NEA

TDB auxiliary data as well as  $S_m^\circ(\text{Sn}, \beta, 298.15 \text{ K}) = (51.18 \pm 0.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_m^\circ(\text{SnO}, \text{tetr.}, 298.15 \text{ K}) = (57.15 \pm 0.20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  selected by this review.

The potential values measured with cell 1 result in

$$\Delta_f G_m^\circ(\text{SnO}, \text{tetr.}, 298.15 \text{ K}) = -(257.23 \pm 0.67) \text{ kJ}\cdot\text{mol}^{-1}.$$

When the average potential-difference value of cell 2 measured at 318.07 K is corrected for the new standard state pressure  $p^\circ = 1 \text{ bar}$  and extrapolated to 298.15 K using the approximation

$$\Delta_f G_m^\circ((\text{A.17}), 318.07 \text{ K}) - \Delta_f G_m^\circ((\text{A.17}), 298.15 \text{ K}) = -\Delta T \Delta_f S_m^\circ(\text{A.17})$$

$\Delta_f G_m^\circ(\text{SnO}, \text{tetr.}, 298.15 \text{ K}) = -253.66 \text{ kJ}\cdot\text{mol}^{-1}$  is obtained.

The mean value obtained with cells 1 and 2 ( $- (255.44 \pm 1.78) \text{ kJ}\cdot\text{mol}^{-1}$ ) overlaps with that derived from solubility measurements  $\Delta_f G_m^\circ(\text{SnO}, \text{tetr.}, 298.15 \text{ K}) = - (254.51 \pm 0.57) \text{ kJ}\cdot\text{mol}^{-1}$  [1966MES/IRA].

### [1929MIL2]

The heat capacities of Sn(II) and Sn(IV) oxide, lead dioxide and lead orthoplumbate have been determined from 70 to 300 K and their entropies at 25 °C have been calculated.

### [1930RAN/MUR]

The equilibrium in the hydrolysis of  $\text{SnCl}_2$  has been measured at 25 °C. The Gibbs energy of the solid tin(II) hydroxide chloride, which was presumed to be  $\text{Sn}(\text{OH})\text{Cl}\cdot\text{H}_2\text{O}(\text{s})$ , and the activity coefficients of  $\text{SnCl}_2$  and of  $\text{Sn}^{2+}$  have been calculated.

The data of Randall and Murakami have been carefully measured and meticulously reported. They have been evaluated according to the 1930 state of the art, which was set among others by Randall (see Table A-4).

Table A-4: Composition of tin(II) hydroxide chlorides [1930RAN/MUR].

Comp.	$\text{Sn}_2\text{Cl}_6(\text{OH})_4\text{O}_6(\text{cr})$ abhurite	$\text{Sn}(\text{OH})\text{Cl}\cdot\text{H}_2\text{O}(\text{s})$	$\text{Sn}(\text{OH})\text{Cl}(\text{s})$	$\text{SnO}(\text{cr})$ romarchite	$\text{Sn}_6\text{O}_4(\text{OH})_4(\text{cr})$ hydroromarchite
w (Sn)	73.45%	62.75%	69.35%	88.12%	84.36%
w (Cl)	16.71%	18.74%	20.71%		
w (O)	9.43%	16.91%	9.35%	11.88%	15.16%
w (H)	0.42%	1.60%	0.59%		0.48%

Unfortunately  $\text{Sn}(\text{OH})\text{Cl}\cdot\text{H}_2\text{O}(\text{s})$  was characterised analytically only and no X-ray data were taken. A thermodynamic analysis of these solubility data using the SIT

model showed that Randall and Murakami investigated in fact  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ , abhurite, see Chapter VIII. As they did not attempt to dry their solid phase, it may have consisted of abhurite plus adhering water and HCl (< 5% relative to  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ ).

### [1932WEI/MIL]

The various modifications of SnO were investigated by X-ray diffraction methods. The precipitated SnO was studied to find out whether it is a hydrous oxide or a hydrous hydrate. The precipitate formed by the interactions of tin(II) salt solutions and ammonia has been found by a temperature-composition isobar and X-ray diffraction studies to be  $2\text{SnO}\cdot\text{H}_2\text{O}$ .

A comparison of this paper with [1922BUR/PAR], [1961DON], [1961DON/MOS], and [1968HOW/MOS] demonstrated how difficult it was to assign the correct structure and formula to hexatin tetrahydroxide tetraoxide  $\text{Sn}_6(\text{OH})_4\text{O}_4(\text{cr})$ .

### [1933HAY]

A solution of 7 M  $\text{SnCl}_2$  was saturated with  $\text{Sn}(\text{OH})_2$  at 80 °C. Regardless of working under air free conditions in the presence of metallic tin the crystallising product always contained Sn(IV). A white microcrystalline powder consisting of hexagonal intergrown flakes was obtained. The analytical results were assumed to be consistent with  $\text{Sn}(\text{OH})_2\cdot\text{SnCl}_2$ , polluted by  $\text{SnO}_2$ .

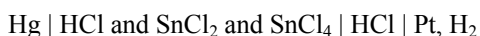
Inspection of Table A-5 shows that the analysis of tin(II) hydroxide chloride represents a challenging problem which has been underestimated by this and other authors. Apparently no reliable empirical formula will be arrived at when only Sn and Cl had been determined, whereas the  $\text{H}_2\text{O}$  content was neglected.

Table A-5: Composition of tin(II) hydroxide chloride [1933HAY].

Composition	Exp.	Exp.	$\text{Sn}(\text{OH})_2\cdot\text{SnCl}_2$	$\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$
	gravimetr. det.	redox. det.		abhurite
w (Sn)	72.3%	67.8%	69.4%	73.45%
w (Cl)	18.3%	18.3%	20.7%	16.71%
n(Sn)/n(Cl)	1.18	1.11	1.00	1.31

### [1934HUE/TAR]

The  $\text{Sn}^{4+}/\text{Sn}^{2+}$  electrode potential was re-determined over a wider range of acid concentration, although the quantity had been studied by [1914FOR/BAR]. The potentials of cells of the following type were measured



and it was attempted to determine thermodynamic quantities of Reaction (A.18)



The  $\text{Sn}^{4+}/\text{Sn}^{2+}$  electrode potential was found to be 0.154 V, which is 8 mV more positive than that given by [1914FOR/BAR].

For a re-evaluation of Huey and Tartar's measurements and the consecutive SIT analysis it is essential to convert the compositional data "Sn, mml. per 1000g. of soln." into molalities. The somewhat cryptic expression – Sn, mml. per 1000g. of soln.– has been translated into millimole  $(\text{Sn})_{\text{tot}}$  ( $\text{SnCl}_2 + \text{SnCl}_4$ ) per 1000g of solution. The symbol  $\mu$  and the unit  $\text{mol}\cdot\text{kg}^{-1}$  has been provisionally assigned to this quantity. The above mentioned conversion has been based on the following relationships:

- 1) Tin has been dissolved in HCl and partially oxidised by  $\text{Cl}_2$   

$$\mu_{\text{Sn}_{\text{tot}}} = \mu_{\text{SnCl}_2} + \mu_{\text{SnCl}_4} .$$
- 2) The molar ratio  $n(\text{Sn(II)})/n(\text{Sn(IV)})$  can be expressed by  $\mu$  or  $m$   

$$\mu_{\text{SnCl}_2} + \mu_{\text{SnCl}_4} = m_{\text{SnCl}_2} + m_{\text{SnCl}_4} .$$
- 3) Mass fractions can also be expressed by  $\mu$  or  $m$   

$$w_{\text{SnCl}_2} = \mu_{\text{SnCl}_2} M_{\text{SnCl}_2} / 1000$$

$$= m_{\text{SnCl}_2} M_{\text{SnCl}_2} / (m_{\text{SnCl}_2} M_{\text{SnCl}_2} + m_{\text{SnCl}_4} M_{\text{SnCl}_4} + m_{\text{HCl}} M_{\text{HCl}} + 1000).$$

The column "Barometric pressure, mm at 0 °C" was treated as follows. The water activities in HCl solutions listed *e.g.* in Table B-1, were used to derive a quadratic function of the equilibrium vapour pressure  $p_{\text{H}_2\text{O}}$  over the pertinent hydrochloric acid solutions  $m_{\text{HCl}}$ . The pressure of the hydrogen  $p_{\text{H}_2}$  was taken as the barometric pressure given in Table I, column 5 [1934HUE/TAR] less the calculated value of  $p_{\text{H}_2\text{O}}$ .

The activity coefficients of the hydrogen ion were calculated according to

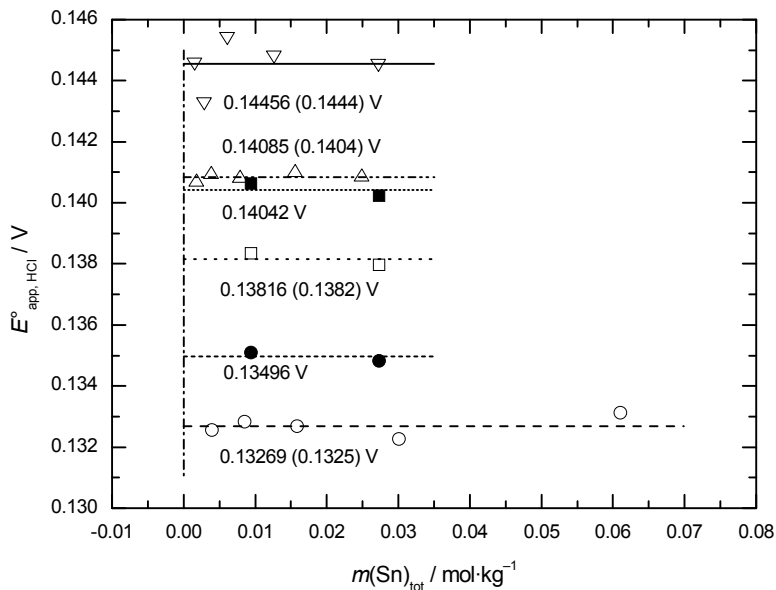
$$\log_{10} \gamma_{\pm, \text{HCl}} = -D + \alpha(\text{H}^+, \text{Cl}^-) \cdot m_{\text{HCl}},$$

and thus  $E_{\text{m(HCl)}}^{\circ'} = E(\text{Sn}^{4+}/\text{Sn}^{2+}) - (k/2) \log_{10} \{m_{\text{Sn(IV)}} p_{\text{H}_2} m_{\text{Sn(II)}}^{-1} a_{\text{H}^+}^{-2}\}$  was obtained.

Figure A-9 shows that at  $m_{\text{HCl}} \geq 0.53$  m  $E_{\text{m(HCl)}}^{\circ'}$  is independent of  $m_{(\text{Sn})_{\text{tot}}}$ , within the scatter of the experimental data.

So far the results of [1934HUE/TAR] were confirmed. A problem arises, however, due to Huey and Tartar's method of extrapolation to  $m_{\text{HCl}} = 0$ . Probably the function  $E_{\text{m(HCl)}}^{\circ'} = E_{\text{m(HCl)}}^{\circ} + b\sqrt{m_{\text{HCl}}}$  was used, although this was not stated explicitly, see Figure A-10. The value,  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.154$  V, given by [1934HUE/TAR] has essentially been reproduced by this kind of curve fitting.

Figure A-9:  $E_m^{\circ'}(\text{HCl})$  of  $\text{Sn}^{4+}/\text{Sn}^{2+}$  vs.  $m(\text{Sn})_{\text{tot}}$ . Experimental data of [1934HUE/TAR]. ( $\circ$ :  $m_{\text{HCl}} = 2.0230 \text{ mol}\cdot\text{kg}^{-1}$ ;  $\square$ :  $m_{\text{HCl}} = 1.1410 \text{ mol}\cdot\text{kg}^{-1}$  and  $t = 25 \text{ }^\circ\text{C}$ ;  $\bullet$ :  $m_{\text{HCl}} = 1.1410 \text{ mol}\cdot\text{kg}^{-1}$  and  $t = 15 \text{ }^\circ\text{C}$ ;  $\blacksquare$ :  $m_{\text{HCl}} = 1.1410 \text{ mol}\cdot\text{kg}^{-1}$  and  $t = 35 \text{ }^\circ\text{C}$ ;  $\triangle$ :  $m_{\text{HCl}} = 0.8512 \text{ mol}\cdot\text{kg}^{-1}$ ;  $\nabla$ :  $m_{\text{HCl}} = 0.5304 \text{ mol}\cdot\text{kg}^{-1}$ , original values in parenthesis).



A SIT analysis was carried out on  $E(\text{Sn}^{4+}/\text{Sn}^{2+})$  by plotting  $E_m^{\circ'}(\text{HCl}) + (k/2) 12D$  vs.  $m_{\text{HCl}}$ , see Figure A-11. The factor  $12D$  was employed because  $a_{\text{H}^+}$  as well as  $p_{\text{H}_2}$  don't need ionic strengths corrections. As pointed out by [1934HUE/TAR] measurements at  $m_{\text{HCl}} < 0.53 \text{ mol}\cdot\text{kg}^{-1}$  deviate from those at  $m_{\text{HCl}} \geq 0.53 \text{ mol}\cdot\text{kg}^{-1}$  owing to hydrolysis reactions of  $\text{Sn}(\text{IV})$  and have been excluded from linear regression. The value

$$E_{m(\text{HCl})}^{\circ'}(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.2077 \pm 0.0015) \text{ V}$$

thus obtained differs considerably from that given by Huey and Tartar.

When  $E_{\text{app,HCl}}^{\circ} + (k/2)\{\log_{10} m_{\text{HCl}} + m\}$  is calculated according to [1972DES/JOV] by assuming that  $m = (2.4 \pm 0.2)$  is independent of ionic strength, the resulting values overlap with the SIT straight line. It should be emphasised, however, that  $E_{\text{app,HCl}}^{\circ} + (k/2)\{\log_{10} m_{\text{HCl}} + m\}$  refers to molality products, whereas  $E_{\text{app,HCl}}^{\circ} + (k/2) 12D$  to activity ones.

Figure A-10:  $E_{m(\text{HCl})}^{\circ'}$  of  $\text{Sn}^{4+}/\text{Sn}^{2+}$  vs.  $m_{\text{HCl}}$ . Extrapolation to  $m_{\text{HCl}} = 0$  by  $E_{m(\text{HCl})}^{\circ'} = E_{m(\text{HCl})}^{\circ'} + b \cdot m_{\text{HCl}}^{0.5}$ . (●: original values of [1934HUE/TAR]; ×:  $E^{\circ} = 0.1564$  V; ○: recalculated values; +:  $E^{\circ} = 0.1567$  V; ○: extrapolated by [1934HUE/TAR] ( $E^{\circ} = 0.1540$  V)).

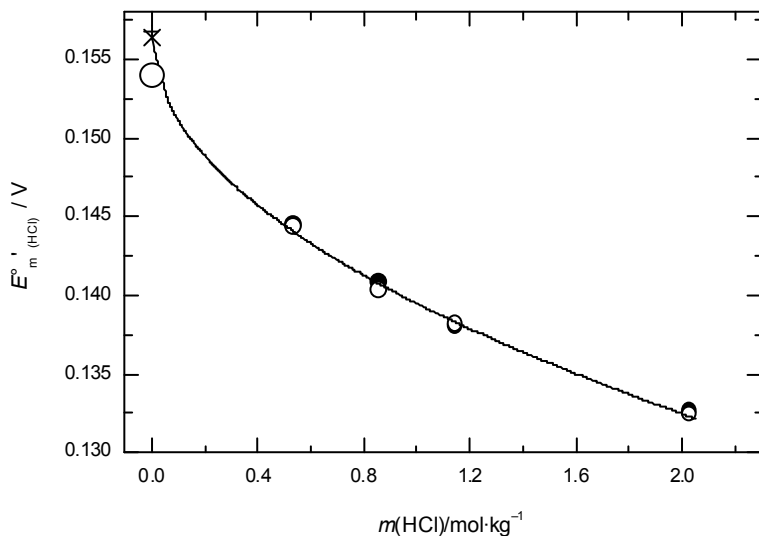
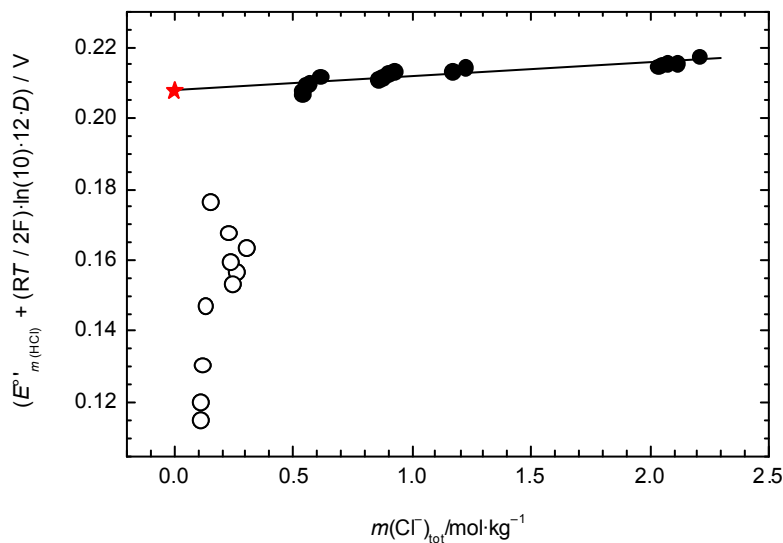


Figure A-11: SIT analysis of  $E(\text{Sn}^{4+}/\text{Sn}^{2+})$  vs.  $m_{\text{Cl}^-}$ , experimental data of [1934HUE/TAR] (●: SIT analysis; ○: not used for regression; ★:  $E_{\text{app}}(\text{Sn(IV)}/\text{Sn(II)}) = (0.2077 \pm 0.0014)$  V).





**[1934PRY]**

Potentiometric measurements were carried out with the cell



- 1) The standard electrode potential  $E^\circ (\text{Sn}^{4+}/\text{Sn})$  was determined at 25 °C,  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.158 \text{ V}$ .
- 2) Measurements with this cell at constant and variable concentration of  $\text{Cl}^-$  and  $\text{SnCl}_4$ , respectively, indicate Nernstian behaviour, *i.e.* a tenfold increase in the  $\text{SnCl}_4$  concentration leads to a decrease of the potential by *ca.* 0.0148 V.
- 3) Increasing activity of  $\text{Cl}^-$  leads to decreasing activity of  $\text{Sn}^{4+}$  (this is obviously due to the formation of Sn(IV) chlorido complexes).
- 4) KCl reduces the  $\text{Sn}^{4+}$  activity more than HCl does, thus KCl was considered to be a stronger complex formation agent than HCl. A more plausible explanation is, however, that HCl partially suppresses the hydroxido complex formation, while KCl does not.

Although this paper seems to be the only one describing direct potentiometric measurements of the reaction



it has not been considered by previous thermodynamic database collections, such as [1999LOT/OCH] and [2002HUM/BER]. The reason for this might be traced back to Latimer's [1952LAT] (p. 149) remark 'Prytz attempted to measure the Sn-Sn<sup>4+</sup> couple in perchlorate solution but we are unable to interpret his (in fact it's her) results'.

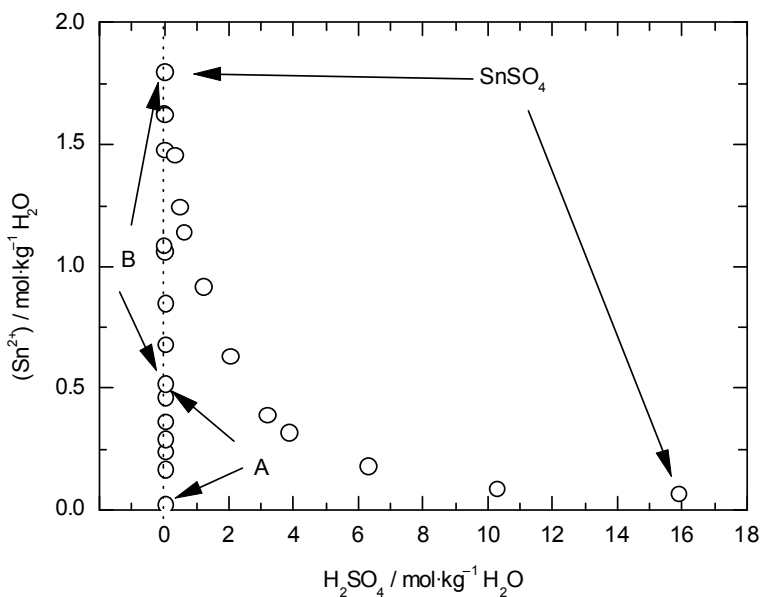
Two sources of errors are indeed obvious. 1) The molality of perchloric acid (0.5 to 1.0 mol·kg<sup>-1</sup>) does not suffice to completely suppress hydrolysis of tin(IV), and 2) spontaneous oxidation of Sn(cr) to Sn<sup>2+</sup> by Sn<sup>4+</sup> should occur. Consequently the actual molality of Sn<sup>4+</sup> is unknown. Thus the result reported by Prytz [1934PRY] has been rejected.

**[1935DEN/KIN]**

A classical phase rule study of the system at 25 and 50 °C with application of Schreinemaker's residue method. Mixture of oxide, sulfuric acid and water had been shaken for at least 3 days (see Figure A-12).

Solid phases at 25 °C: SnSO<sub>4</sub>·2SnO·4H<sub>2</sub>O (A), SnSO<sub>4</sub>·SnO (B), SnSO<sub>4</sub>

at 50 °C: SnSO<sub>4</sub>·2SnO·2H<sub>2</sub>O (A2), SnSO<sub>4</sub>·SnO (B), SnSO<sub>4</sub>.

Figure A-12: The ternary system SnO-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O.

### [1938HAR/WHI]

The activities of tin amalgams from  $x(\text{Sn}) = 0$  to  $x(\text{Sn})_{\text{sat}}$ , the solubility of Sn(s) in Hg(l) and of Hg in Sn(s), and the standard potential of  $\text{Sn}^{2+}/\text{Sn}$  were determined at 25 °C. These aims were accomplished by:

- 1) measuring cells of the type  $\text{Sn}(\text{Hg})_1 | \text{SnCl}_2, \text{HCl} | \text{Sn}(\text{Hg})_2$ ;
- 2) direct analysis and application of the Nernst equation;
- 3) measuring of cells of the types :

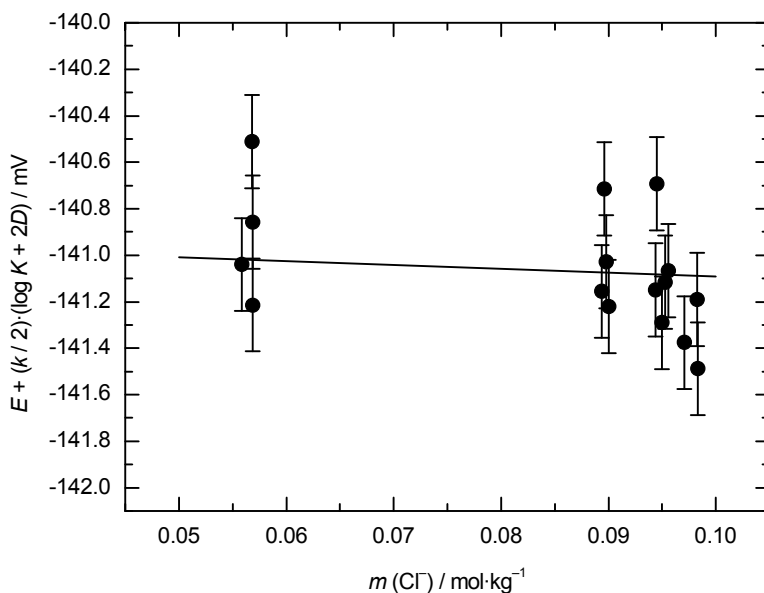


where  $x = 100 y$ ;  $(E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ(\text{Sn}^{2+}/\text{Sn}(\text{Hg})_{\text{sat}})) = -(1.0 \pm 0.1) \text{ mV}$ ,  $x_{\text{Sn}}^1(\text{Hg}) = 0.01263$ ,  $x_{\text{Sn}}^s(\text{Hg}) = 0.925$ ,  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) = -(140.6 \pm 0.2) \text{ mV}$ .

The suspected disadvantage of these carefully and well designed measurements was that  $\text{Sn}^{2+}$  might undergo complex formation in chloride containing media. A recalculation with ChemSage, using a preliminary set of  $\varepsilon$  values and hydroxido and chlorido complex formation constants, confirmed this assumption. An attempt to analyze the experimental cell-potential data according to the SIT approach failed, because in fact essentially only 2 different chloride molalities were investigated (see Figure A-13). A standard potential  $E^\circ(\text{Sn}^{2+}/\text{Sn}(\text{Hg})_{\text{sat}}, 298.15 \text{ K}) = -(140.97 \pm 0.64)$

mV was obtained. With the activity of tin in a saturated amalgam,  $a_{\text{Sn}} = 0.927$ , given by [2003YEN/GRO] this results in  $E^\circ (\text{Sn}^{2+}/\text{Sn}(0), 298.15 \text{ K}) = -(140.00 \pm 0.64) \text{ mV}$ .

Figure A-13: Variation of  $E + (k/2) \log_{10} K + 2D$  vs.  $m_{\text{Cl}^-}$  (●: experimental data; solid line: linear fit (Chemsage supported calculation)).



One remark with respect to Haring and White's analysis of their data must be made. The reported value of  $(E^\circ (\text{Sn}^{2+}/\text{Sn}(0)) - E^\circ (\text{Sn}^{2+}/\text{Sn}(\text{Hg})_{\text{sat}}) = -(1.0 \pm 0.1) \text{ mV}$  has, according to [2003YEN/GRO], the wrong sign.

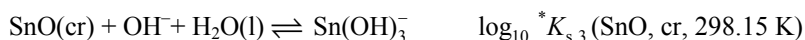
### [1939GOR]

The hydrolysis of tin(II) perchlorate in diluted perchloric acid has been investigated by adding NaOH solution and measuring the pH with a hydrogen electrode at 298 K.

In this paper the formation of the trinuclear hydroxido complex  $\text{Sn}_3(\text{OH})_4^{2+}$  was not considered, therefore the reported data were re-evaluated for the purpose of this review. This indicated that the tin(II) aqua ion is much stronger acid than expected from other literature data. This is probably due to the partial oxidation of tin(II) [1958TOB]. Therefore, the reported data were rejected by the reviewers.

**[1941GAR/HEI]**

The experimental data of [1941GAR/HEI] were re-evaluated, taking into account the formation constants of the tin(II) hydroxido and chlorido complexes selected by this review. The re-evaluation of the solubility of SnO(cr) in hydrochloric acid solutions, in pure water under oxygen-free conditions, and in sodium hydroxide solutions led to the following three solubility constants reported here.

*Solubility of SnO(s) in HCl solutions*

Garrett and Heiks [1941GAR/HEI] prepared SnO(s) by reacting tin(II) chloride solutions with sodium hydroxide solutions and thereby precipitating tin(II) hydroxide. The tin(II) hydroxide was dehydrated in warm conductivity water containing a small amount of sodium hydroxide. The results of six analyses gave an average  $100w(\text{Sn}) = 87.6$  for the Sn content of the solid phase (theoretically:  $100w(\text{Sn}) = 88.123$ ). The solubility of SnO was determined in dilute solutions of HCl ( $[\text{HCl}]_{\text{ini}} = 4.4 \times 10^{-4} - 9.6 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ ). The total concentration of the dissolved tin(II) was determined by a polarographic method and by redox titrations using  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. An attempt was made to approach equilibrium from supersaturation and undersaturation by reacting SnO(s) with HCl solutions at 35 °C and 25 °C for several days, respectively. Then the sample pairs were both thermostated at 25 °C for a total of seven days. Provided SnO(s) is more soluble at 35 °C than at 25 °C and the 35 °C samples reached equilibrium before they were cooled to 25 °C equilibrium was approached from supersaturation in those experiments indeed. The usefulness of this method has been questioned [1963SCH].

The re-evaluation (see Figure VII-8) resulted in  $\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{SnO}, \text{cr}, 298.15 \text{ K}) = -(253.11 \pm 1.38) \text{ kJ}\cdot\text{mol}^{-1}$  which is equivalent to  $\log_{10} {}^*K_{s,0} = (2.00 \pm 0.24)$  for Reaction (A.20), when the selected  $\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.39 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -(237.14 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$  from the NEA auxiliary data is taken into account.

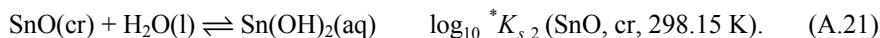


Three deficiencies need to be criticised in this work. (1) The observed quantities are the total molality of Sn(II) and the initial molality of HCl. Information on the equilibrium pH or molality of free  $\text{Sn}^{2+}$  values would have facilitated the re-evaluation and improved the precision of the measurement. (2) Dissolution of SnO(s) in dilute HCl leads to hydroxido and chlorido complex formation, thus at least 4 species contribute appreciably to the total molality of Sn(II). Consequently the accuracy of the  $\log_{10} {}^*K_{s,0}$  (A.20) determination depends largely on the accuracy of the respective

complex formation constants. (3) The solid tin(II) oxide has not been characterised by taking its X-ray powder diffraction pattern, thus the identity of the actually investigated phase has not yet been unambiguously ascertained.

#### *Solubility of SnO(s) in H<sub>2</sub>O*

The value of the solubility product  $^*K_{s,2}$  (SnO, cr, 298.15 K) was determined by equilibrating SnO(cr), prepared as described above, with H<sub>2</sub>O under oxygen-free conditions:



$$\log_{10} {}^*K_{s,2}(\text{SnO, cr, 298.15 K}) = -(5.30 \pm 0.13).$$

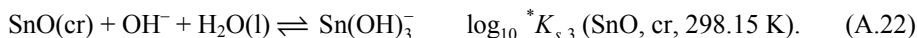
The solubility of SnO(cr) in H<sub>2</sub>O is listed in Table A-6.

Table A-6: Solubility of SnO(cr) in H<sub>2</sub>O.

$10^6 \cdot m_{\text{Sn(II)}}/\text{mol} \cdot \text{kg}^{-1}$	$\log_{10}(m_{\text{Sn(II)}}/\text{mol} \cdot \text{kg}^{-1})$	$\sigma$
5.82	- 5.235	$\pm 0.068$
5.82	- 5.235	$\pm 0.068$
4.66	- 5.332	$\pm 0.029$
4.32	- 5.365	$\pm 0.062$
4.49	- 5.348	$\pm 0.045$
Mean value:	- 5.303	$2\sigma \pm 0.126$

#### *Solubility of SnO(s) in NaOH solutions*

The value of  $^*K_{s,3}$  (SnO, cr, 298.15 K) was determined by equilibrating SnO(cr), prepared as described above, with sodium hydroxide solutions ( $[\text{NaOH}]_{\text{ini}} = 0.05$  to 1.13 m):



The experimental data in alkaline solutions were re-evaluated using the SIT approach, see Table A-7. Again an attempt was made to approach equilibrium from supersaturation and undersaturation. As  $\Delta z^2 = 0$  for Reaction (A.22), the Debye-Hückel term vanishes in the course of ionic strength corrections. The activity of water was estimated from molality based osmotic coefficients  $\varphi_m$  [1959ROB/STO] in the range of  $0 < m_{\text{NaOH}} < 1.2$  by  $\log_{10} a_{\text{H}_2\text{O}} = A \cdot m_{\text{NaOH}}$ , where  $A = -0.0149 \text{ kg} \cdot \text{mol}^{-1}$ . Plotting and linear regressing of  $\log_{10} \{ {}^*K_{s,3} / a_{\text{H}_2\text{O}} \}$  vs.  $m_{\text{Na}^+}$  results in intercept

$$\log_{10} {}^*K_{s,3}^0(\text{SnO, cr, 298.15 K}) = -(0.84 \pm 0.02)$$

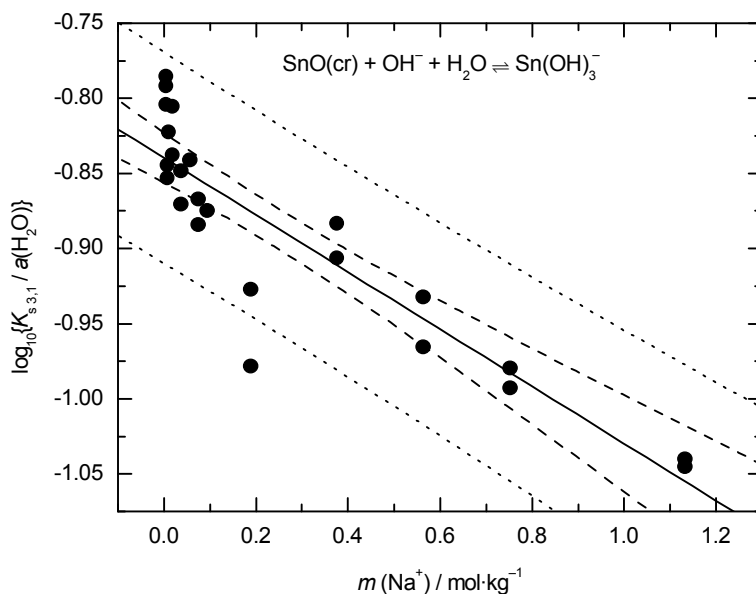
and slope  $\Delta \varepsilon = (0.16 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$  ( $\Delta \varepsilon = \alpha(\text{Na}^+, \text{Sn}(\text{OH})_3^-) - \alpha(\text{Na}^+, \text{OH}^-)$ ), see Figure A-14. In addition  $\log_{10} K_3^0 = (4.46 \pm 0.13)$  ( $\text{Sn}(\text{OH})_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{Sn}(\text{OH})_3^-$ )

was evaluated assuming  $\alpha(\text{Sn}(\text{OH})_2, \text{NaOH}) = 0$ . Using the NEA TDB value of  $(0.04 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$  for  $\alpha(\text{Na}^+, \text{OH}^-)$ ,  $\alpha(\text{Na}^+, \text{Sn}(\text{OH})_3^-) = (0.20 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$  can be obtained.

Table A-7: Solubility of SnO(cr) in NaOH solutions.

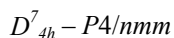
$10^3 \cdot m_{\text{NaOH}} / \text{mol} \cdot \text{kg}^{-1}$	$10^5 \cdot m_{\text{Sn(II)}} / \text{mol} \cdot \text{kg}^{-1}$	$\log_{10} a(\text{H}_2\text{O})$	$\log_{10} (^*K_{33} / a(\text{H}_2\text{O}))$
5.0000	67.9000	-0.0001	-0.8036
5.0000	70.5000	-0.0001	-0.7847
5.0000	69.6000	-0.0001	-0.7912
7.6400	95.7000	-0.0001	-0.8439
7.6400	94.1000	-0.0001	-0.8523
10.2300	134.0000	-0.0002	-0.8216
18.7400	238.0000	-0.0003	-0.8369
18.7400	254.0000	-0.0003	-0.8044
36.9700	440.0000	-0.0006	-0.8688
36.9700	460.0000	-0.0006	-0.8468
55.4000	700.0000	-0.0008	-0.8389
55.4000	700.0000	-0.0008	-0.8389
73.4000	880.0000	-0.0011	-0.8647
73.4000	850.0000	-0.0011	-0.8817
93.1000	1100.0000	-0.0014	-0.8716
93.1000	1100.0000	-0.0014	-0.8716
187.9000	1800.0000	-0.0028	-0.9721
187.9000	2000.0000	-0.0028	-0.9212
375.8000	4200.0000	-0.0056	-0.8946
375.8000	4400.0000	-0.0056	-0.8718
563.1000	6000.0000	-0.0084	-0.9151
563.1000	5600.0000	-0.0084	-0.9485
751.0000	7300.0000	-0.0112	-0.9567
751.0000	7100.0000	-0.0112	-0.9700
1131.0000	9700.0000	-0.0169	-1.0109
1131.0000	9800.0000	-0.0169	-1.0060

Figure A-14: Solubility of SnO(cr) in NaOH solutions (●: experimental data; solid line: linear fit ( $\log_{10}^* K_{s31} = -(0.840 \pm 0.016)$ ,  $\Delta\varepsilon = (0.190 \pm 0.038)$  kg·mol<sup>-1</sup>); dashed lines: confidence limits; dotted lines: prediction limits).



#### [1941MOO/PAU]

Powder photographic X-ray data are used to show that the tetragonal crystals SnO and PbO have similar structures:



$$\text{SnO: } a_0 = (3.796 \pm 0.006), c_0 = (4.816 \pm 0.008) \text{ \AA}, Z = 2$$

$$\text{PbO: } a_0 = (3.947 \pm 0.006), c_0 = (4.988 \pm 0.008) \text{ \AA}, Z = 2.$$

The density of SnO(tetr.) calculated from the unit cell data amounts to  $\rho = (6447 \pm 31)$  kg·m<sup>-3</sup>.

#### [1942GOR/LEI]

Data on the solubility of SnO(s) in aqueous solutions of 0.0113 to 0.1125 M HClO<sub>4</sub> are presented at 25 °C. The solubilities in HClO<sub>4</sub> and HCl (according to [1941GAR/HEI]) are identical within the experimental error up to [Sn(II)] = 0.05 M. The authors took this as evidence for the absence of significant chloride complexing by Sn<sup>2+</sup> in this concentration range.

As the perchlorate ion is not capable of forming complexes with  $\text{Sn}^{2+}$  this study is potentially very interesting.

The solubility determining species in the acid range investigated is  $\text{Sn}^{2+}$ , whereas  $\text{SnOH}^+$  and  $\text{Sn}_3(\text{OH})_4^{2+}$  are responsible for only 5 to 10% of dissolved Sn(II). When three reactions participate in a dissolution process it is far more reliable to base the stability constant determination on experiments in homogeneous solution, e.g. [1958TOB], [1976GOB].

Consequently the re-evaluation of Gorman and Leighton's data was based on the stability constants selected by this Review. For comparison with [1941GAR/HEI] the data were transformed to the molality basis. The re-evaluation (see Figure VII-9) led to the same result as [1941GAR/HEI]:

$$\Delta_f G_m^\circ (\text{SnO, cr, 298.15 K}) = -(253.29 \pm 1.38) \text{ kJ}\cdot\text{mol}^{-1}$$

which is equivalent to

$$\log_{10} {}^* K_{s,0} (\text{SnO, cr, 298.15 K}) = (2.05 \pm 0.24)$$

for Reaction (A.23), when the selected  $\Delta_f G_m^\circ (\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.39 \pm 0.30) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f G_m^\circ (\text{H}_2\text{O, l, 298.15 K}) = -(237.14 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$  from the NEA auxiliary data are taken into account.



This work suffers from two methodological deficiencies. (1) The pH values of the equilibrated solutions were not measured. Thus information on the concentration of free  $\text{H}^+$  can be obtained from the analytical charge balance only, but this depends on all reactions participating in the dissolution process. As the evaluation has to be based on the initial molality of  $\text{HClO}_4$  and the equilibrium molality of Sn(II), it is necessarily less precise. (2) The solid tin(II) oxide studied has not been characterised by taking its X-ray powder diffraction pattern, thus the identity of the actually investigated phase has not been unambiguously ascertained.

### [1947RYS/TUR]

Solubility determinations in the system  $\text{HCl-SnCl}_2\text{-H}_2\text{O}$  at 5, 15 and 25 °C had been performed at concentrations of HCl from 2 to 10%. Results are tabulated. Also results from [1888ENG] at 0 °C are listed and discussed as not in agreement with this work.

Solubility experiments were performed in a thermostat rotating the closed tubes "over-head" for 3 hours. Previous experiments from sub- and supersaturation confirmed equilibrium after 2-3 h. After density determination the liquid samples were titrated for  $\text{Sn}^{2+}$  (iodometrically) and for total acid with NaOH against phenolphthalein in boiling solutions. Solid phase composition was determined by Schreinemakers method yielding the dihydrate in all cases.



No solubility experiments in pure water were tried due to hydrolysis, but it was attempted to fix the eutectic temperature ( $t = -6.8\text{ }^\circ\text{C}$  and 37.9% SnCl<sub>2</sub>). Points on the ice curve are given at ( $-6.25\text{ }^\circ\text{C}$ , 36.8%) and ( $-6.45\text{ }^\circ\text{C}$ , 37.3% SnCl<sub>2</sub>).

Approximate solubility data are plotted for 0 °C from measurements in a company lab.

Temperature variation given as  $\pm 0.05\text{ K}$ . Evidence for equilibrium is given, but no explicit information that oxidation of tin(II) was avoided in starting material and during experiments.

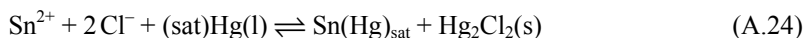
### [1947SAP/KOH]

SnO in the solid state is unstable, disproportionation according to  $4\text{SnO} \rightarrow \text{Sn}_3\text{O}_4 + \text{Sn}$  is observed between 400 and 1040 °C. Molten SnO, however, is stable. Melts of the composition SnO are obtained if cold pellets of SnO or SnC<sub>2</sub>O<sub>4</sub> are introduced into Al<sub>2</sub>O<sub>3</sub> crucibles heated to approximately 1200 °C. Melts of similar appearance are obtained if mixtures of Sn and SnO<sub>2</sub> (1:1) or SnO<sub>2</sub> and C (1:1) are treated similarly. SnO forms a yellow Sn(II) silicate glass with SiO<sub>2</sub> at 1000 °C. Neither Sn nor SnO<sub>2</sub> reacts similarly with SiO<sub>2</sub>. The SnO melts solidify at 1040 °C; this is also the temperature at which the disproportionation begins on cooling. In comparison with Sn and SnO<sub>2</sub>, SnO is very volatile; the boiling point is estimated to be approximately 1700 °C. The thermal properties of SnO are compared with those of CO, SiO, and GeO.

### [1949RIC/POP]

Composition and stabilities of Sn(II)-chlorido complexes were investigated polarographically in KCl solutions.

From the half-wave potential of the reaction  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}(0)$  vs. the normal calomel electrode according to Reaction (A.24)



and the standard potential of Reaction (A.25)



and accounting for  $a_{\text{Sn}}$  in a saturated tin amalgam [2003YEN/GRO], the half-cell potential for  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{cr})$  was determined in 1 M KCl solutions. For Reaction (A.24),  $E^\circ$  (1 M KCl, 298.15 K) = -433 mV and for Reaction (A.25)  $E^\circ$  (1 M KCl, 298.15 K) = -278 mV are reported. This leads to a half-cell potential for  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{cr})$  of  $E_c^{\circ'}(I = 1.0\text{ M KCl}, 25\text{ }^\circ\text{C}) = -(154.03 \pm 2.00)\text{ mV}$ . The uncertainty of  $\pm 2\text{ mV}$  has been estimated by this review. With a value for  $\varepsilon(\text{Sn}^{2+}, \text{Cl}^-) = (0.14 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$ , Eq. (II.35), and Eq. (VI.5) lead to:

$$E_m^{\circ}(\text{Sn}^{2+}/\text{Sn}) = E_c^{\circ'} + \left( \frac{RT \ln(10)}{nF} \right) \cdot \left[ \sum \nu_i \cdot \log_{10} \left( \frac{m_{\text{KCl}}}{c_{\text{KCl}}} \right) + 2D + \Delta\varepsilon \cdot m_{\text{Cl}^-} \right]$$

where  $\sum \nu_i = 1$ ,  $\Delta \varepsilon = 2\varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{Sn}^{2+}, \text{Cl}^-)$ .

Thus  $E^\circ(\text{Sn}^{2+}/\text{Sn}(0), 298.15 \text{ K}) = -(138.44 \pm 3.70) \text{ mV}$  has been obtained.

It should be noted, however, that a value of  $E^\circ(1 \text{ M KCl}, 298.15 \text{ K}) = -(280.1 \pm 0.2) \text{ mV}$  is reported for Reaction (A.25) by [1961IVE/JAN]. Moreover, the same remark applies as made in the Appendix A entry for [1970BON/TAY].

The polarographic behaviour of tin(II) in  $\text{LiClO}_4$  (0.09 to 2.65 M) and KCl (0.1 to 4.0 M) solutions was studied under  $\text{CO}_2$  atmosphere. From the measurements made in  $\text{LiClO}_4$  solutions the authors determined the standard polarographic reduction potential corresponding to the  $\text{Sn}^{2+}/\text{Sn}$  reduction, as discussed above. The dependence of the half-wave potential on the chloride ion concentration was explained by the formation of four chlorido complexes ( $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$ ,  $\text{SnCl}_3^-$  and  $\text{SnCl}_4^{2-}$ ). The temperature applied for the measurements is ambiguous. In Tables 1 to 3, which contain the primary data,  $t = 16 \text{ }^\circ\text{C}$  is given, but during the calculations the authors used the value of 0.0591 for  $RT/\ln(10)/nF$ , which corresponds to  $25 \text{ }^\circ\text{C}$ . The reported thermodynamic formation constants were derived using the Debye-Hückel equation, which is not compatible with the SIT. More importantly, it seems that no acid was added to the solutions and the hydrolysis of tin(II) was not considered during the evaluation of the experimental data. Since the pH of the solutions is not reported, the re-evaluation of the experimental data is not possible, therefore the reported data on tin(II) chlorido complexes were not considered further in this review.

### [1950DUK/COU]

Potentiometric measurements, using the concentration cell method, have been performed to study the complex formation between tin(II) and chloride ion at  $25 \text{ }^\circ\text{C}$  in 2.03 M  $\text{HClO}_4$  medium. The authors concluded the formation of four chlorido complexes:  $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$ ,  $\text{SnCl}_3^-$  and  $\text{SnCl}_4^{2-}$ . Both [1961RAB/MOO] and [1961TOB/HUG] re-evaluated the experimental data reported in [1950DUK/COU] and reported the formation of only three chlorido complexes ( $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$  and  $\text{SnCl}_3^-$ ). The chloride ion concentration varied up to 0.85 M, which corresponds to 42% replacement of the background electrolyte. This resulted in notable change of the activity coefficients during the measurements, therefore the experimental data were re-evaluated for the purposes of this review using the half of the data ( $[\text{Cl}^-] = 0$  to 0.4 M). A further deficiency of the experiments in [1950DUK/COU] is that the total concentration of tin(II) was not held constant and no information is provided concerning the degree of dilution. Assuming no dilution, the recalculated formation constants are as follows:  $\log_{10} \beta_1 = (1.08 \pm 0.20)$ ,  $\log_{10} \beta_2 = (1.76 \pm 0.20)$ ,  $\log_{10} \beta_3 = (1.4 \pm 0.40)$ . Assuming 1 M or 2 M chloride concentration in the titrant solution  $\log_{10} \beta_1 = (1.07 \pm 0.20)$ ,  $\log_{10} \beta_2 = (1.43 \pm 0.20)$  ( $\log_{10} \beta_3$  is rejected by the computer program Psequad) and  $\log_{10} \beta_1 = (1.07 \pm 0.20)$ ,  $\log_{10} \beta_2 = (1.67 \pm 0.20)$  ( $\log_{10} \beta_3$  is rejected) can be calculated, respectively. In other words, if the  $[\text{Sn}^{2+}]_{\text{tot}}$  decreases during the

measurements no appreciable amount of  $\text{SnCl}_3^-$  can be detected in the solution, and the value of  $\log_{10} \beta_2$  is also strongly affected. Considering the above facts, only  $\log_{10} \beta_1 = (1.07 \pm 0.4)$  will be considered further in this review.

### [1951DUK/PIN]

The reaction rate between Fe(III) and Sn(II) has been studied as a function of the halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) concentrations at 25 °C in 2.03 M  $\text{HClO}_4$  medium. The authors concluded that a minimum of three halide ions (bound to the reacting Fe(III) and Sn(II) ions in total) are required to be added to the activated complex for any appreciable reaction rate, and more halides considerably enhance the possibility of the reaction. The order of increasing effectiveness is  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , which is probably due to the increasing ease of oxidation of the halide ions.

The formation constants of the complexes  $\text{SnCl}^+$  and  $\text{SnBr}^+$  derived in this work can be only regarded as a rough approximation, therefore an uncertainty of  $\pm 0.5$  has been assigned to the reported  $\log_{10} \beta_1$  values.

### [1951POW/LAT]

The standard partial molar entropies of monatomic ions and of non-electrolytes in aqueous solutions can be represented by empirical expressions, for monatomic ions the following equation has been found to be valid:

$$S_m^\circ / \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.5 \cdot (R / \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \cdot \ln (M / \text{g} \cdot \text{mol}^{-1}) + 37 - 270 \cdot z \cdot (\text{\AA} / r_e)^2$$

where  $z$  is the absolute value of the charge on the ion,  $M$  the molar mass and  $r_e$  the effective radius of the ion. For cations  $r_e / \text{\AA} = 2.0 + r_x / \text{\AA}$ ,  $r_x$  being the crystal radius.

In Table A-8 partial molar entropies of monoatomic ions, its uncertainties and the respective references as well as the effective ionic radii,  $r_x$  ('IR'), given by Shannon [1976SHA] are listed. The Powell-Latimer equation has been fitted to these data, weighted by uncertainties of entropies. The uncertainties of  $S_m^\circ (\text{Cr}^{3+})$  and  $S_m^\circ (\text{Th}^{4+})$  have been estimated according to the discussion in [1976DEL/HAL] and set equal to the uncertainty of  $S_m^\circ (\text{Zr}^{4+})$  [2005BRO/CUR], respectively. Slightly modified coefficients were obtained for the Powell-Latimer equation.

$$S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 1.5 \cdot (R / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \cdot \ln (M / \text{g} \cdot \text{mol}^{-1}) + (156.84 \pm 0.26) - (1237.62 \pm 2.14) \cdot z \cdot (\text{\AA} / r_e)^2$$

It should be emphasised that aqua americium(III) and aqua uranium(IV) ion appear twice in this correlation, with the conventional coordination number  $n = 6$  and those coordination numbers assigned to them by [1992SAS/SHO], namely  $n = 8$  and  $n = 9$ , respectively.

Table A-8: Standard molar entropy of monoatomic cations calculated with the Powell-Latimer equation.

Cation	$n$	$z$	$r_x/\text{\AA}$	$M/\text{g mol}^{-1}$	$z/(2+r_x)^2$	$S_m^\circ - 1.5 \cdot R \cdot \ln(M)$	$\pm \Delta S_m^\circ$	$S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Ag <sup>+</sup>	6	1	1.150	107.8682	0.1008	15.07	0.40	73.45 <sup>(a)</sup>
Li <sup>+</sup>	6	1	0.760	6.941	0.1313	-11.92	0.15	12.24 <sup>(a)</sup>
Na <sup>+</sup>	6	1	1.020	22.9898	0.1096	19.35	0.15	58.45 <sup>(a)</sup>
K <sup>+</sup>	6	1	1.380	39.0983	0.0875	55.48	0.20	101.20 <sup>(a)</sup>
Rb <sup>+</sup>	6	1	1.520	85.4678	0.0807	66.27	0.25	121.75 <sup>(a)</sup>
Cs <sup>+</sup>	6	1	1.670	132.9054	0.0742	71.12	0.50	132.10 <sup>(a)</sup>
Tl <sup>+</sup>	6	1	1.500	204.3833	0.0816	59.15	3.50	125.50 <sup>(b)</sup>
Sn <sup>2+</sup>	6	2	1.180	118.71	0.1978	-76.27	4.00	-16.70 <sup>(a)</sup>
Pb <sup>2+</sup>	6	2	1.190	207.2	0.1965	-48.02	1.00	18.50 <sup>(a)</sup>
Zn <sup>2+</sup>	6	2	0.740	65.409	0.2664	-161.94	0.50	-109.80 <sup>(a)</sup>
Cd <sup>2+</sup>	6	2	0.950	112.411	0.2298	-131.69	1.50	-72.80 <sup>(a)</sup>
Hg <sup>2+</sup>	6	2	1.020	200.59	0.2193	-102.31	0.80	-36.19 <sup>(a)</sup>
Cu <sup>2+</sup>	6	2	0.730	63.546	0.2683	-149.78	4.00	-98.00 <sup>(a)</sup>
Mg <sup>2+</sup>	6	2	0.720	24.305	0.2703	-176.79	4.00	-137.00 <sup>(a)</sup>
Ca <sup>2+</sup>	6	2	1.000	40.078	0.2222	-102.23	1.00	-56.20 <sup>(a)</sup>
Sr <sup>2+</sup>	6	2	1.180	87.62	0.1978	-87.28	2.00	-31.50 <sup>(c)</sup>
Ba <sup>2+</sup>	6	2	1.350	137.327	0.1782	-52.99	2.00	8.40 <sup>(c)</sup>
Am <sup>2+</sup>	7	2	1.210	243.0614	0.1941	-69.51	15.00	-1.00 <sup>(c)</sup>
Ni <sup>2+</sup>	6	2	0.690	58.6934	0.2764	-182.59	1.40	-131.80 <sup>(d)</sup>
Cr <sup>3+</sup>	6	3	0.620	51.9961	0.4370	-367.26	21.00	-317.98 <sup>(e)</sup>
Al <sup>3+</sup>	6	3	0.535	26.981	0.4668	-366.09	10.00	-325.00 <sup>(a)</sup>
U <sup>3+</sup>	6	3	1.025	238.0289	0.3278	-256.422	13.9	-188.172 <sup>(c)</sup>
Np <sup>3+</sup>	6	3	1.010	237.0482	0.3311	-261.783	20.3	-193.584 <sup>(c)</sup>
Pu <sup>3+</sup>	6	3	1.000	244.0642	0.3333	-253.073	6.154	-184.510 <sup>(c)</sup>
Am <sup>3+</sup>	6	3	0.975	243.0614	0.3389	-269.51	15.00	-201.00 <sup>(c)</sup>
Am <sup>3+</sup>	8	3	1.090	243.0614	0.3142	-269.51	15.00	-201.00 <sup>(f)</sup>
U <sup>4+</sup>	6	4	0.890	238.0289	0.4789	-485.145	12.6	-416.895 <sup>(c)</sup>
U <sup>4+</sup>	9	4	1.050	238.0289	0.4210	-485.1455	12.6	-416.895 <sup>(f)</sup>
Np <sup>4+</sup>	6	4	0.870	237.0482	0.4856	-494.589	12.4	-426.390 <sup>(c)</sup>
Pu <sup>4+</sup>	6	4	0.860	244.0642	0.4890	-483.098	10.2	-414.535 <sup>(c)</sup>
Am <sup>4+</sup>	6	4	0.850	243.0614	0.4925	-474.51	21.00	-406.00 <sup>(c)</sup>
Zr <sup>4+</sup>	6	4	0.720	91.224	0.5406	-546.86	35.20	-490.57 <sup>(g)</sup>
Th <sup>4+</sup>	9	4	1.090	232.0381	0.4189	-490.53	35.00	-422.60 <sup>(h)</sup>

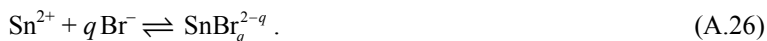
References: (a): [1989COX/WAG]; (b): [2005OLI/NOL]; (c): [2003GUI/FAN]; (d): [2005GAM/BUG]; (e): [1976DEL/HAL]; (f): [1992SAS/SHO]; (g): [2005BRO/CUR]; (h): [1982WAG/EVA].

**[1952LAT]**

Latimer's classical compilation "The oxidation state of the elements and their potentials in aqueous solutions" is still an indispensable reference book for thermodynamic data. Appendix III "Methods for the estimation of entropy values" provided valuable information for the estimation of the standard partial molar entropy of  $\text{Sn}^{4+}(\text{aq})$  by referring to [1951POW/LAT].

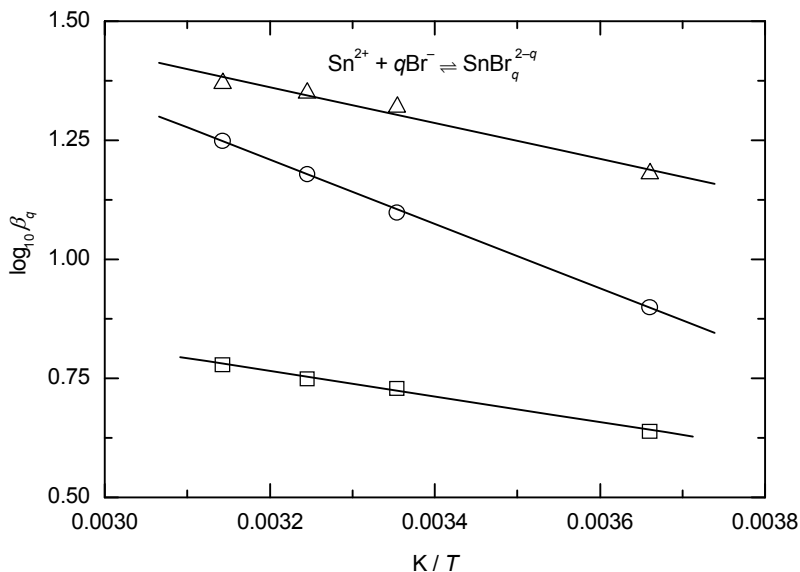
**[1952VAN]**

The experimental work is very similar to [1952VAN/RHO]. Potentiometric measurements using the concentration cell method have been performed to investigate the complex formation between tin(II) and bromide ion in 3 M  $\text{NaClO}_4$  medium ( $[\text{Sn}^{2+}]_{\text{tot}} = 10 \text{ mM}$ ,  $[\text{Br}^-]_{\text{tot}} = 0 \text{ to } 0.5 \text{ M}$ ). The author applied several different hydrogen ion concentrations ( $[\text{H}^+]_{\text{tot}} = 0.1 \text{ to } 0.5 \text{ M}$ ) and four different temperatures (0, 25, 35 and 45 °C). Analogously to [1952VAN/RHO], the slightly different experimental data obtained at different hydrogen ion concentrations were explained by the formation of two hydrolysed species ( $\text{Sn}(\text{OH})^+$  and  $\text{Sn}(\text{OH})\text{Br}(\text{aq})$ ) beside the three mononuclear bromido complexes ( $\text{SnBr}^+$ ,  $\text{SnBr}_2(\text{aq})$  and  $\text{SnBr}_3^-$ ). As explained in the comments on [1952VAN/RHO], no hydrolysis of tin(II) should be considered at  $[\text{H}^+]_{\text{tot}} \geq 0.1 \text{ M}$ . Therefore, the experimental data reported in [1952VAN] were re-evaluated for the purposes of this review assuming that the differences between the measurements performed at different  $[\text{H}^+]_{\text{tot}}$  concentrations are due to some unknown experimental errors. At the worst 33% of the background electrolyte was replaced during the measurements, due to the substitution of  $\text{NaClO}_4$  by both  $\text{HClO}_4$  and  $\text{NaBr}$ . Although no apparent medium effect was observed by [1961TOB/HUG] under similar conditions, considering the above mentioned experimental errors and the fact that the author listed rounded values of the experimental data, an uncertainty of  $\pm 0.3$  has been assigned to the recalculated  $\log_{10} \beta_q$  values. These constants (Table VIII-12) were used to derive enthalpies of the Reactions ((A.26),  $q = 1, 2, 3$ ) at  $I = 3 \text{ M}$ :



The  $\log_{10} \beta_q - 1/T$  plots are depicted in Figure A-15. The slopes of the straight lines correspond to  $\Delta_r H_m((\text{A.26}), q) = (5.1 \pm 2.0)$ ,  $(12.9 \pm 2.0)$  and  $(7.2 \pm 4.0)$   $\text{kJ}\cdot\text{mol}^{-1}$ , for  $q = 1, 2$  and  $3$  respectively.

Figure A-15: Temperature dependence of  $\log_{10} \beta_q$  ((A.26),  $q = 1, 2, 3$ ) recalculated from [1952VAN] ( $\square$ :  $\log_{10} \beta_1$ ,  $\circ$ :  $\log_{10} \beta_2$ ,  $\triangle$ :  $\log_{10} \beta_3$ ).

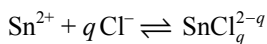


### [1952VAN/RHO]

The concentration cell

$\text{Sn}(\text{Hg, satd}) \mid x \text{ M Sn}(\text{ClO}_4)_2, y \text{ M HClO}_4, (3-2x-y-z) \text{ M NaClO}_4, z \text{ M NaCl} \parallel x \text{ M Sn}(\text{ClO}_4)_2, y \text{ M HClO}_4, (3-2x-y) \text{ M NaClO}_4 \mid \text{Sn}(\text{Hg, satd})$

was used to measure the equilibrium constants for the reactions

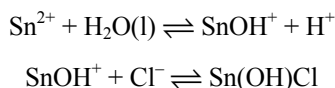


at 0, 25, 35, 45 °C and at constant ionic strength  $I = 3 \text{ M NaClO}_4$  ( $[\text{Sn}^{2+}]_{\text{tot}} = 10 \text{ mM}$ ,  $[\text{Cl}^-]_{\text{tot}} = 0 \text{ to } 0.6 \text{ M}$ ) at two  $[\text{H}^+]_{\text{tot}}$  concentrations (0.1 and 0.5 M). The experimental data were first treated by assuming three mononuclear chlorido complexes ( $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$  and  $\text{SnCl}_3^-$ ). However, significantly different formation constants were calculated from the data obtained at different  $[\text{H}^+]_{\text{tot}}$  concentrations. This difference was explained by the hydrolysis of tin(II), and the authors suggested the formation of two additional species:  $\text{Sn}(\text{OH})^+$ ,  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$ .

The first hydrolysis constant calculated in [1952VAN/RHO] ( $\log_{10} \beta_{1,1}^{\circ} = -1.7$ ) is much higher than that obtained by Tobias [1958TOB] or Gobom [1976GOB] under similar conditions. The experimental data reported in [1952VAN/RHO] were

later re-evaluated by Rabideau and Moore [1961RAB/MOO] who rejected the formation of hydroxido complexes [1961RAB/MOO]. Moreover, Tobias and Hugus [1961TOB/HUG] demonstrated experimentally, that in the solutions with  $[H^+]_{\text{tot}} = 0.05$  to 0.5 M no hydrolysis of tin(II) should be considered [1961TOB/HUG].

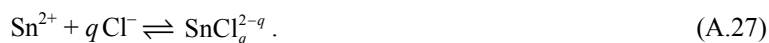
The constants of the reactions



were evaluated from the variation of the cell data with acidity, and were recalculated on the basis of the data given in Table 2 [1952VAN/RHO], the results could be reproduced only approximately. As the total  $\text{Sn}^{2+}$  concentration was not varied polynuclear complex formation cannot be excluded. The experimental data were explained with 5 complex formation constants, *i.e.* for  $\text{SnOH}^+$ ,  $\text{Sn}(\text{OH})\text{Cl}$ ,  $\text{SnCl}^+$ ,  $\text{SnCl}_2$ ,  $\text{SnCl}_3^-$ . The values for the formation constants of  $\text{SnOH}^+$  and  $\text{Sn}(\text{OH})\text{Cl}$  can only be regarded as tentative.

Therefore, the experimental data reported in [1952VAN/RHO] were re-evaluated for the purposes of this review assuming that the differences between the measurements performed at different  $[H^+]_{\text{tot}}$  concentrations are due to some unknown experimental errors. Due to the replacement of  $\text{NaClO}_4$  by both  $\text{HClO}_4$  and  $\text{NaCl}$ , up to 37% of the background electrolyte was substituted during the measurements. Although no apparent medium effect was observed by [1961TOB/HUG] under similar conditions, considering the above mentioned unknown experimental errors an uncertainty of  $\pm 0.3$  has been assigned to the recalculated  $\log_{10} \beta_q$  values (see Table VIII-9).

The temperature dependence of the formation constants allowed us to calculate the reaction enthalpy for the formation of  $\text{SnCl}_q^{2-q}$  ( $q = 1, 2, 3$ ) complexes:



From the plot in Figure A-16,  $\Delta_r H_m((\text{A.27}), q = 1) = (9.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r H_m((\text{A.27}), q = 2) = (14.1 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r H_m((\text{A.27}), q = 3) = (17.2 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$  can be derived.

### [1953HUM/OBR]

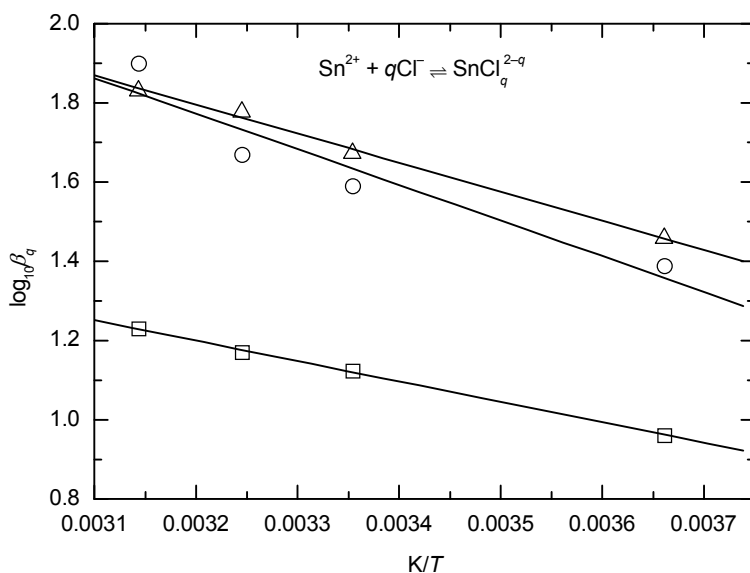
The enthalpies of formation of tin(II) oxide and tin(IV) oxide at 298.16 K were determined by combustion calorimetry of Reactions (A.28) and (A.29) at 303.16 K.



The authors were careful in synthesising the  $\text{SnO}$  sample, and their final sample was heated in hydrogen at 220 to 256 °C for 4 hours. The product after this treatment gave  $w_{\text{SnO}} = 99.5\%$ ,  $w_{\text{H}_2\text{O}} = 0.18\%$  and  $w_{\text{CO}_2} = 0.10\%$ , leaving 0.15% undetermined. There was evidence of the presence of  $\text{Sn}(\text{IV})$  oxide which probably

accounts for the bulk of this 0.15% (If the numerical values of  $w_{\text{SnO}}$ ,  $w_{\text{H}_2\text{O}}$  and  $w_{\text{CO}_2}$  are correct, then the undetermined rest,  $w(\text{rest}) = 0.22\%$ , but this probably doesn't change the results significantly). There was a contamination  $w_{\text{Si}} = 0.014\%$ .

Figure A-16: Temperature dependence of  $\log_{10} \beta_q$  ((A.27),  $q = 1, 2, 3$ ) recalculated from [1952VAN/RHO] ( $\square$ :  $\log_{10} \beta_1$ ,  $\triangle$ :  $\log_{10} \beta_2$ ,  $\circ$ :  $\log_{10} \beta_3$ ).



The energy equivalent of the calorimeter was determined with benzoic acid. The unburned tin of Reaction (A.28) ranged from 1.02 to 4.11% of the total, and the respective corrections were made in the heat measurement. Corrections for impurities of the tin were applied. Combustion according to Reaction (A.29) was 100% complete, and X-ray diffraction of the combustion product gave only lines corresponding to tetragonal tin(IV) oxide. Corrections for the water, carbon dioxide and tin(IV) oxide contents of the tin(II) oxide were made. In addition all measurements were corrected to unit fugacity of oxygen, to constant pressure, and to 298.16 K.

The enthalpies of formation of tin(II) oxide and tin(IV) oxide were found to be

$$\Delta_f H_m^\circ (\text{SnO, tetr., 298.15 K}) = -(285.98 \pm 0.67) \text{ kJ}\cdot\text{mol}^{-1} \text{ and}$$

$$\Delta_f H_m^\circ (\text{SnO}_2, \text{tetr., 298.15 K}) = -(580.82 \pm 0.33) \text{ kJ}\cdot\text{mol}^{-1}.$$

The possibility to recalculate these results is rather limited, because the authors do not report to which measurements the different corrections for unburned tin have to be assigned. It seemed, however, justified to use currently valid molar masses for tin and tin(II) oxide. From the five determinations of the enthalpy of Reaction (A.29) it can



be concluded that the uncertainty is  $1\sigma$ ; in the recalculated values this is changed to  $2\sigma$ . The recalculated values are:

$$\Delta_f H_m^\circ (\text{SnO, tetr., 298.15 K}) = - (286.00 \pm 1.34) \text{ kJ}\cdot\text{mol}^{-1} \text{ and}$$

$$\Delta_f H_m^\circ (\text{SnO}_2, \text{tetr., 298.15 K}) = - (580.85 \pm 0.67) \text{ kJ}\cdot\text{mol}^{-1}.$$

### [1953KIN/TOD]

This paper presents the results of low-temperature heat capacity measurements of both tin(II) and tin(IV) sulphides using adiabatic calorimetry. Both compounds show normal heat capacity curves, except that at temperatures below 80 K,  $\text{SnS}_2$  has the lower molar heat capacity.

The measured heat-capacity data of  $\alpha$ -SnS listed in Table A-9 were approximated by cubic splines, see Figure A-17. The extrapolated portions, between 0 and the first measured value, were evaluated by means of the empirical sum of Debye (Eq. (A.30) and Einstein (Eq. (A.31)) functions with  $\Theta_D = 146$  K and  $\Theta_E = 311$  K.

$$C_{V,D}/R = 9(T/\Theta_D)^3 \int_0^{\Theta_D/T} y^4 e^y (e^y - 1)^{-2} dy \quad (\text{A.30})$$

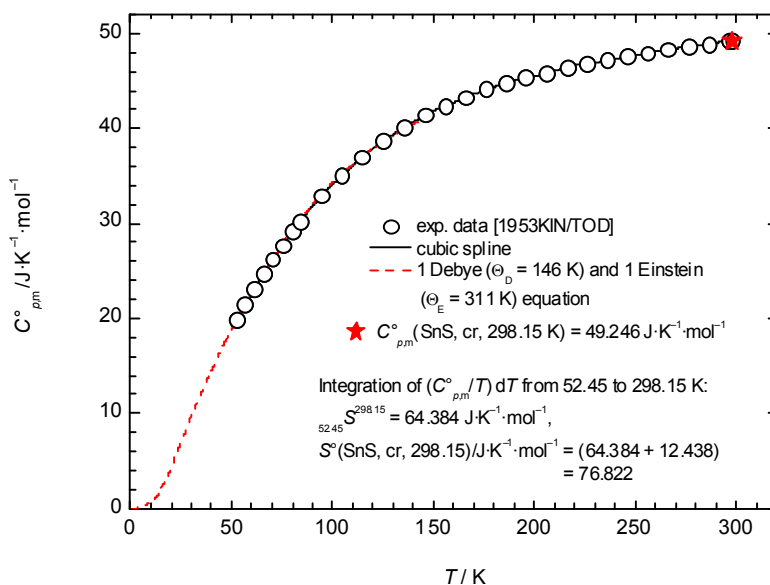
$$C_{V,E}/R = 3(\Theta_E/T)^2 \exp(\Theta_E/T) / [\exp(\Theta_E/T) - 1]^2 \quad (\text{A.31})$$

This sum fits the measured heat capacities to within 1% and for the temperature range 51 to 170 K, see Figure A-17.

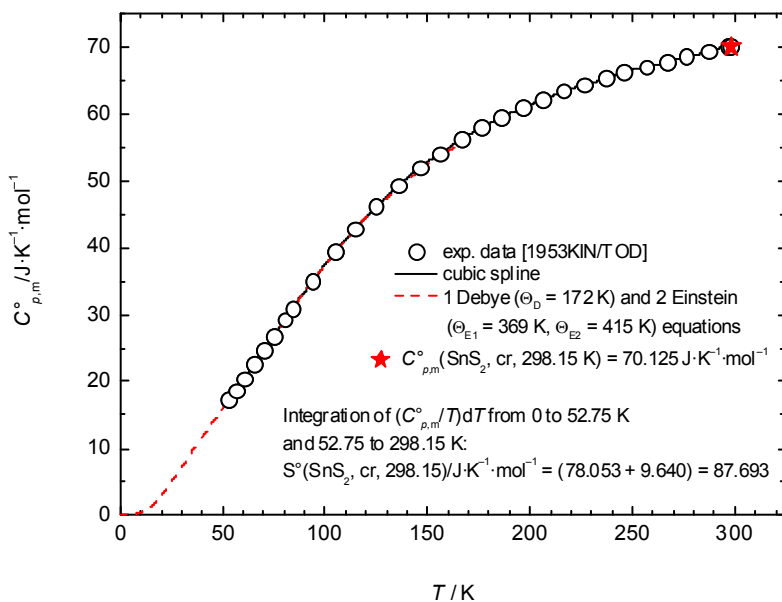
The measured heat-capacity data of  $\text{SnS}_2(\text{cr})$  listed in Table A-10 were evaluated analogously, but this time the sum of one Debye function with  $\Theta_D = 172$  K and two Einstein functions with  $\Theta_{E1} = 369$  K and  $\Theta_{E2} = 415$  K were employed for extrapolation from 0 to the first temperature where  $C_{p,m}^\circ$  has been measured. This sum fits the measured heat capacities to within 1% and for the temperature range 51 to 170 K, see Figure A-18.

Table A-9: Heat capacities of  $\alpha$ -SnS.

$T/\text{K}$	$C_{p,m}^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
52.45	19.924	114.7	36.974	216.37	46.442
56.82	21.401	125.28	38.698	226.05	46.819
61.4	23.117	136.01	40.196	236.31	47.196
65.9	24.769	146.22	41.426	246.03	47.572
70.49	26.263	155.93	42.384	256.19	47.907
75.28	27.711	166.03	43.263	266.05	48.325
80.2	29.179	176.12	44.099	276.36	48.576
83.71	30.158	186.09	44.727	286.68	48.911
94.67	32.920	195.91	45.355	296.8	49.246
104.47	35.012	206.31	45.815	298.15	49.246

Figure A-17: Low temperature heat-capacity function of  $\alpha$ -SnS.Table A-10: Heat capacities of  $\text{SnS}_2(\text{cr})$ .

$T/\text{K}$	$C_{p,m}^o/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}^o/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}^o/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
52.75	17.318	114.65	42.844	216.55	63.429
56.45	18.631	124.72	46.108	226.55	64.350
60.65	20.393	135.98	49.371	236.88	65.354
65.17	22.548	146.13	52.007	246.21	66.275
70.05	24.686	155.79	54.057	257.06	67.028
74.92	26.807	166.54	56.234	266.82	67.8234
80.28	29.188	176.14	57.948	276.28	68.576
84.04	30.907	186.22	59.580	287.38	69.371
93.66	34.962	196.28	60.919	296.54	70.124
105.07	39.476	206.63	62.216	298.15	70.124

Figure A-18: Low temperature heat-capacity function of SnS<sub>2</sub>(cr).

The results of the authors were essentially confirmed by this review, see values in parentheses.

$$C_{p,m}^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 49.25 \quad (49.25)$$

$$S_m^{\circ}(\text{SnS}, \alpha, 298.15 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (77.0 \pm 0.8) \quad (76.82)$$

$$C_{p,m}^{\circ}(\text{SnS}_2, \text{cr}, 298.15 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 70.12 \quad (70.13)$$

$$S_m^{\circ}(\text{SnS}_2, \text{cr}, 298.15 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (87.4 \pm 0.8) \quad (87.69)$$

### [1954BRU]

The author investigated the spectral change of Sn(IV) observed in 1 to 17 M H<sub>2</sub>SO<sub>4</sub> solutions. At 240 nm, the author observed a continuous decrease of adsorbance up to 7 M H<sub>2</sub>SO<sub>4</sub>, but above this concentration the spectral intensities increased again. He concluded that the first spectral change corresponds to the equilibrium  $\text{Sn}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Sn}(\text{SO}_4)_2(\text{aq})$ , and determined  $\log_{10} \beta_2 = -0.85$  (apparently neglecting the changing ionic strength between 1 and 7 M H<sub>2</sub>SO<sub>4</sub>). This conclusion was reconsidered in [1957BRU] (see Appendix A). The second step of spectral change was attributed to the equilibrium  $\text{Sn}(\text{SO}_4)_2(\text{aq}) + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{Sn}(\text{SO}_4)_3(\text{aq})$ .

**[1954SCH/DAV]**

The formation of tin(II)- and tin(IV)-fluoride complexes were studied by a polarographic method in 0.8 M NaNO<sub>3</sub> and 2.5 M KNO<sub>3</sub> media at 298.15 K. The authors also studied the redox potential of the reactions  $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \beta\text{-Sn}$  and  $\text{Sn}^{2+} \rightleftharpoons \text{Sn}^{4+} + 2\text{e}^-$  in 0.04 to 3.0 M (Na/H)ClO<sub>4</sub> media.

The half-wave potentials of the reduction measured under inert atmosphere at different fluoride concentrations ( $[\text{F}^-] = 0.005$  to  $0.75$  M at  $I = 0.8$  M, and  $[\text{F}^-] = 0.1$  to  $2.5$  M at  $I = 2.5$  M) were used to evaluate the formation constant of the  $\text{SnF}_3^-$  species, which was assumed to be the only complex present in the solution. This assumption is correct only for  $[\text{F}^-] \geq 0.25$  M. In addition, the background electrolytes (NaNO<sub>3</sub> or KNO<sub>3</sub>) were entirely replaced by NaF/KF during the measurements, which resulted in substantial medium effect. Therefore a part of the experimental data ( $[\text{F}^-] \leq 0.2$  M at  $I = 0.8$  M and  $[\text{F}^-] \leq 0.7$  M at  $I = 2.5$  M) was re-evaluated for the purpose of this review (assuming that the activity coefficients do not change significantly up to 20% replacement of the background electrolyte). The following formation constants were obtained:  $\log_{10} \beta_2 = (7.91 \pm 0.27)$  ( $3\sigma$ ),  $\log_{10} \beta_3 = (9.78 \pm 0.12)$  at  $I = 0.8$  M, and  $\log_{10} \beta_3 = (10.76 \pm 0.24)$  at  $I = 2.5$  M. Under the conditions used practically no free metal ion is present in the solutions; therefore the formation of the different tin(II)-nitrate complexes were neglected in this calculation.

An attempt was made to study the tin(IV) complexes fluoride solutions containing dissolved sodium stannate, but poorly defined, irreversible waves were detected at  $\approx 1.2$  V. Alternatively, the anodic waves in acidified fluoride solutions (0.1 M KF + 0 to 0.1 M HF) were studied to obtain some information on the tin(IV) complexes. From these data the authors estimated  $\log_{10} \beta_6 \approx 25$  for the formation of complex  $\text{SnF}_6^{2-}$ .

**[1955BRU]**

The solubility of SnO<sub>2</sub>(s) has been determined in 0.2 to 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions at 30 and at 18 °C.  $[\text{Sn(IV)}]_{\text{tot}}$  was determined spectrophotometrically at 230, 240 and 250 nm. The experimental data were explained by the reaction



Estimated activity coefficients were used to determine the thermodynamic equilibrium constant for the above reaction. In strongly acidic solutions SnO<sub>2</sub>(s) may dissolve as partially hydrolyzed complexes ( $\text{Sn(OH)}^{3+}$ ,  $\text{Sn(OH)}_2^{2+}$ ,  $\text{Sn(OH)}_3^+$  and oligonuclear species). Although the author verifies that these hydroxido complexes alone cannot result in the experimentally observed solubility, he did not consider the simultaneous presence of the sulfato and hydroxido complexes and, the possible formation of mixed hydroxido-sulfato complexes. Moreover, besides  $\text{SO}_4^{2-}$ , the  $\text{HSO}_4^-$  anion may also form complexes with the cations present in the solution. Consequently, the equilibrium system is more complicated than Brubaker claimed. Since the formation

constants of the binary hydroxido complexes are unknown, the re-evaluation of the experimental data reported in [1955BRU] is not possible.

### [1956BAB/LIS]

The authors determined solubilities of the sulfides of tin, antimony and bismuth in basic solutions by exploiting the peculiarity of these sulfides to form very stable colloidal suspensions. Definite volumes with known contents of dispersed solid sulfide were added to the solution of given pH. Solubility was then estimated from the volume of suspension when the solution remained turbid after stirring for 4 – 4.5 h. Results at 20 °C are listed. The pH of solutions was obviously established with NaOH.

In alkaline sulfide solutions the formation of  $\text{SnS}_3^{2-}$  is reported. Although the generally accepted reaction in NaOH is  $3\text{SnS}_2 + 6\text{OH}^- \rightleftharpoons 2\text{SnS}_3^{2-} + \text{Sn}(\text{OH})_6^{2-}$ , the authors claimed the formation of  $\text{SnS}_2(\text{OH})^-$  in alkaline solutions.

The method used for the determination of the concentration in the colloidal  $\text{SnS}_2$  suspension is not described (the authors stated that a 'standard' method was applied). The ionic strength was probably not controlled (the solutions contained an unknown amount of acetate-ammonia buffer). The authors used  $\log_{10} K_1 = 14.92$  and  $\log_{10} K_2 = 7.24$  for the protonation constants of sulfide ion in their calculation. Since the currently accepted first protonation constant is much higher ( $\log_{10} K_1 = (19 \pm 2)$ ), the reported experimental data were re-evaluated for the purposes of this review ( $\log_{10} K ((\text{A.32}), 293.15 \text{ K}) = (9.13 \pm 0.09)$ ).



Table A-11: Solubility of  $\text{SnS}_2$  in M.

pH	8	9	10	11	12
Solubility/M	$< 10^{-5}$	$2.0 \times 10^{-5}$	$1.5 \times 10^{-4}$	$1.4 \times 10^{-3}$	$1.4 \times 10^{-2}$

A plot of the data in double logarithmic scale gives a straight line. Authors claim a reproducibility of  $10^{-4}$  to  $10^{-5}$  M. From the finely dispersed state of the sulfide an enhanced solubility can be expected compared to mineral samples. No further description of the  $\text{SnS}_2$  preparation itself is given.

Due to the insufficiency of the experimental details and the high uncertainty of the first protonation constant of sulfide ion, the reviewers assigned considerably higher uncertainty to the above constant ( $\pm 2.0$ , see Table IX-1). For these reasons, the re-evaluated constants cannot be used to derive a selected value.

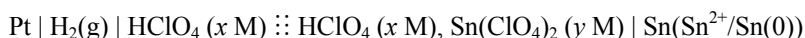
**[1957BRU]**

In this paper the author reinvestigated the spectral change of Sn(IV) observed in 1 to 4 M H<sub>2</sub>SO<sub>4</sub> solutions (already studied in [1954BRU]). He concluded that the spectral change observed in this concentration range is related to the equilibrium  $\text{SnSO}_4^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{Sn}(\text{SO}_4)_2(\text{aq})$  ( $K_2$ ). Using estimated activity coefficients he calculated the thermodynamic equilibrium constant for the above reaction ( $\log_{10} K_2^\circ \approx 2$ ). Considering the constants reported in [1955BRU] for the equilibrium  $\text{Sn}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Sn}(\text{SO}_4)_2(\text{aq})$  ( $\log_{10} \beta_2 = -0.85$ ),  $K_2 \gg K_1$  can be calculated, for which the author did not provide explanation. The author confirmed that the spectral change reported in [1954BRU] for  $c_{\text{H}_2\text{SO}_4} > 6$  M corresponds to the equilibrium  $\text{Sn}(\text{SO}_4)_2(\text{aq}) + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{Sn}(\text{SO}_4)_3(\text{aq})$ .

**[1957WAK/SAL]**

The behaviour of electroplated tin and tin-amalgam electrodes in solutions of varying pH, initially free from tin ions, has been examined from the extreme acid to the extreme alkaline range, and the probable existence of an oxide film on the surface of metals has been discussed. A new technique was described for measuring the potential of Sn<sup>2+</sup>/Sn under air-free conditions.

In the context of this review the evaluation of the standard potential of tin, attempted by these authors, is of particular interest. The cell used was of the type:



where  $y \ll x$ , thus the liquid junction potential was considered negligible. The measurements were carried out under strictly air-free conditions and, for comparison, without this extreme protection as well.

Unfortunately the actually measured  $E$  values of cell (Sn<sup>2+</sup>/Sn(0)) were not given, only the  $E^\circ$  values were, see Table A-12. The former have been retrieved by inverting the procedure used by [1957WAK/SAL] 'Following the procedure of [1923LEW/RAN] for calculating the activity coefficient of various ionic strengths....'. For this recalculation analytical functions  $\log_{10} \gamma_{\text{H}^+} = f_{\text{H}}(I)$  and  $\log_{10} \gamma_{\text{Sn}^{2+}} = f_{\text{Sn}}(I)$  were derived from [1927LEW/RAN], Table 8., pp.329-330, and finally the Nernst equation was employed:

$$E = E^\circ - (RT/2F) \log_{10} ((m_{\text{H}^+} \gamma_{\text{H}^+})^2 \cdot (m_{\text{Sn}^{2+}} \gamma_{\text{Sn}^{2+}})^{-1}).$$

A SIT analysis with the potential values thus obtained resulted in  $E^\circ = -(0.1394 \pm 0.0005)$  V, see Figure A-19. In view of the assumptions necessary to reproduce the original experimental data set, the uncertainty was increased so that the value accepted for statistical analysis

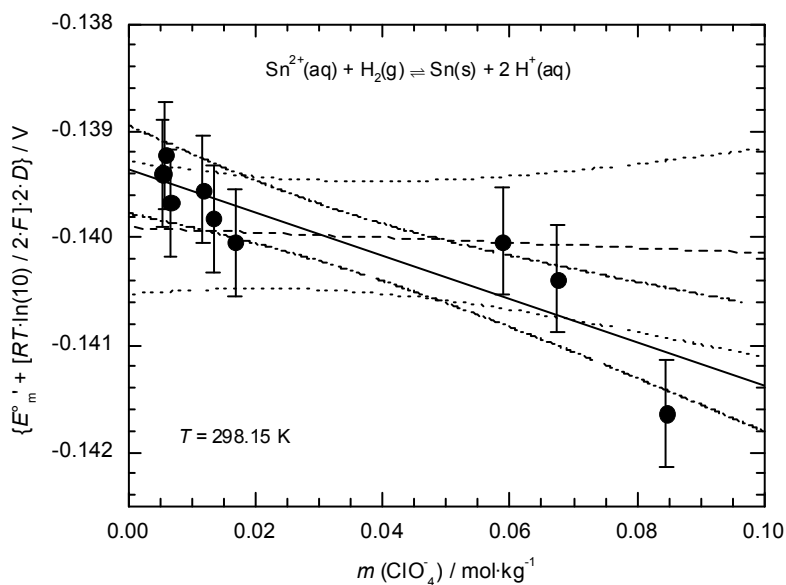
$$E^\circ = -(0.1394 \pm 0.0015) \text{ V}$$

overlaps with that given by the authors ( $E^\circ = -(0.1375 \pm 0.0005)$  V). Due to the limited range of  $m_{\text{ClO}_4^-}$  considered, no reliable  $\Delta\varepsilon$  value could be extracted from these measurements. When the slope was fixed to  $-0.09 RT \ln(10)/2F$ , as predicted by  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-)$  selected by this review and  $\varepsilon(\text{H}^+, \text{ClO}_4^-)$  given in Appendix B, Table B-4, a value of  $E^\circ = -(0.1399 \pm 0.0006)$  V was arrived at, see Figure A-19. This value falls just outside the confidence limits of the one accepted for statistical analysis.

Table A-12: Standard potential  $E^\circ$  of the reaction  $\text{Sn}^{2+} + \text{H}_2(\text{g}) \rightleftharpoons \beta\text{-Sn} + 2\text{H}^+$ .

HClO <sub>4</sub> /M	Sn(ClO <sub>4</sub> ) <sub>2</sub> /M	$E^\circ$ /V air-free	$E^\circ$ /V recalc.	HClO <sub>4</sub> /m	Sn(ClO <sub>4</sub> ) <sub>2</sub> /m	<i>I</i> /m	ClO <sub>4</sub> <sup>-</sup> /m
0.005	0.00021	-0.1376	-0.11400	0.005016	0.000213	0.00565	0.00544
0.005	0.00042	-0.1374	-0.10501	0.005016	0.000425	0.00629	0.00587
0.005	0.00085	-0.1378	-0.09672	0.005016	0.000852	0.00757	0.00672
0.010	0.00085	-0.1375	-0.11500	0.010035	0.000852	0.01259	0.01174
0.010	0.00170	-0.1377	-0.10659	0.010036	0.001705	0.01515	0.01345
0.010	0.00340	-0.1378	-0.09830	0.010037	0.003412	0.02027	0.01686
0.050	0.00425	-0.1370	-0.13879	0.050286	0.004273	0.06311	0.05883
0.050	0.00850	-0.1370	-0.13061	0.050306	0.008551	0.07596	0.06741
0.050	0.01700	-0.1373	-0.12359	0.050347	0.017117	0.10170	0.08458

Figure A-19: SIT analysis of the data of [1957WAK/SAL] (●: experimental data recalculated by this review; solid line: linear fit; dotted lines: 95% confidence limits; dashed line: slope predicted by  $\Delta\varepsilon = 0.08 \text{ kg}\cdot\text{mol}^{-1}$ ).



**[1958KOV]**

The solubility product of “tin(II) hydroxide” defined by



was determined by a polarographic method at 22 °C to be  $\log_{10} K_{s,0}^{\circ} = -28.1$ .

The author claims to have measured pH and concentration of  $\text{Sn}^{2+}$  at the beginning of “ $\text{Sn(OH)}_2\text{(s)}$ ” precipitation from chloride solution. Separately precipitated tin(II) hydroxide was analysed and found to have a molar ratio  $n(\text{Sn})/n(\text{OH}) = 1/2$  and was contaminated by traces of chloride only. However, this does not mean that the precipitate had this composition when the reverse of Reaction (A.33) commenced. The extremely low value of  $\log_{10} K_{s,0}^{\circ}$  seems to indicate that  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$  [1981SCH/NES] was the initial product. When the data of [1930RAN/MUR] are analysed assuming “ $\text{Sn(OH)}_2\text{(s)}$ ” precipitation the corresponding value would be  $\log_{10} K_{s,0}^{\circ} = -28.56$ .

**[1958ORR/CHR]**

In this paper high temperature enthalpy increments for tin(II) sulphide (see Table A-13) and tin(IV) sulphide (see Table A-14) were determined by drop calorimetry.

Table A-13: SnS, measured enthalpy increments above 298.15 K.

<i>T</i> /K	$[H^{\circ}-H^{\circ}(0)]/\text{J}\cdot\text{mol}^{-1}$	<i>T</i> /K	$[H^{\circ}-H^{\circ}(0)]/\text{J}\cdot\text{mol}^{-1}$	<i>T</i> /K	$[H^{\circ}-H^{\circ}(0)]/\text{J}\cdot\text{mol}^{-1}$
388.4	15247	764.9	35707	980.3	49263
389.9	15331	793.7	37673	1071	54451
482.4	20058	843.6	40769	1114.1	57087
483.6	20142	863.6	42192	1122.5	59932
580.5	25414	868.1	42652	1143.8	73070
604.5	26586	872.8	42903	1161.4	91438
675.7	30686	876.3	43531	1185.1	93195
726.6	33573	892.1	44368	1225.1	96249

Table A-14: SnS<sub>2</sub>, measured enthalpy increments above 298.15 K.

<i>T</i> /K	$[H^{\circ}-H^{\circ}(298)]/\text{J}\cdot\text{mol}^{-1}$	<i>T</i> /K	$[H^{\circ}-H^{\circ}(298)]/\text{J}\cdot\text{mol}^{-1}$	<i>T</i> /K	$[H^{\circ}-H^{\circ}(298)]/\text{J}\cdot\text{mol}^{-1}$
400	7155	592	21338	980.3	49263
489.6	13640	594.9	21757	1071	54451
491.2	13807	603.1	22217	1114.1	57087
498.7	14435	621.6	23723	1122.5	59932
524	16150	692.6	29121	1143.8	73070
561.2	19037	762.1	34476	1161.4	91438



The original entries  $H^\circ - H^\circ(298.15 \text{ K})$  for SnS were converted to  $H^\circ - H^\circ(0 \text{ K})$  in order to compare the measured data directly with the calculations of Wiedemeier *et al.* [1980WIE/CSI2].  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] = 10770 \text{ J}\cdot\text{mol}^{-1}$  was taken from [1958ORR/CHR]. The enthalpy increments of Table A-13 are represented to within the average limits indicated by the equations, see also Figure A-20.

SnS( $\alpha$ ) (0.2%, 298–875 K):

$$[H^\circ(T) - H^\circ(298.15 \text{ K})]/\text{J}\cdot\text{mol}^{-1} = 35.69T/\text{K} + 1.565 \times 10^{-2}(T/\text{K})^2 - 3.77 \times 10^5(T/\text{K})^{-1} - 10770;$$

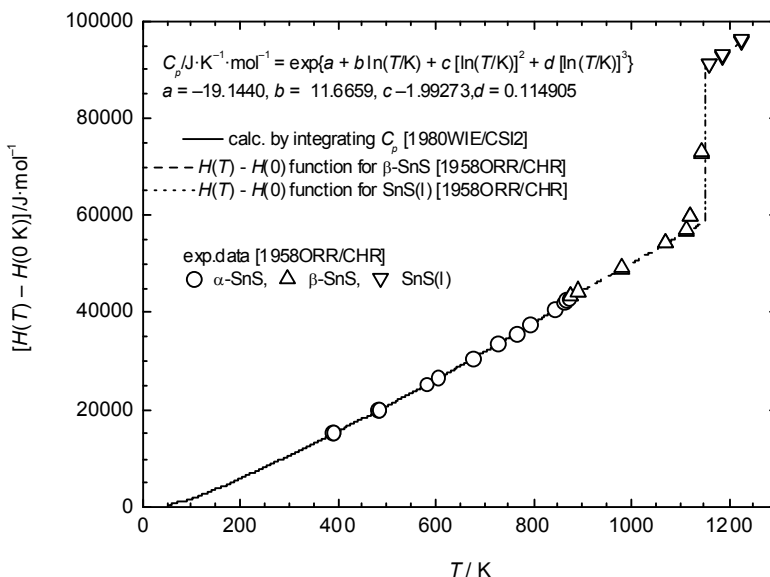
SnS( $\beta$ ) (0.1%, 875–1153 K):

$$[H^\circ(T) - H^\circ(298.15 \text{ K})]/\text{J}\cdot\text{mol}^{-1} = 40.92T/\text{K} + 7.82 \times 10^{-3}(T/\text{K})^2 - 9121;$$

SnS(l) (0.1%, 1153–1250 K):

$$[H^\circ(T) - H^\circ(298.15 \text{ K})]/\text{J}\cdot\text{mol}^{-1} = 74.89T/\text{K} - 6318.$$

Figure A-20: Enthalpy function of SnS(cr).



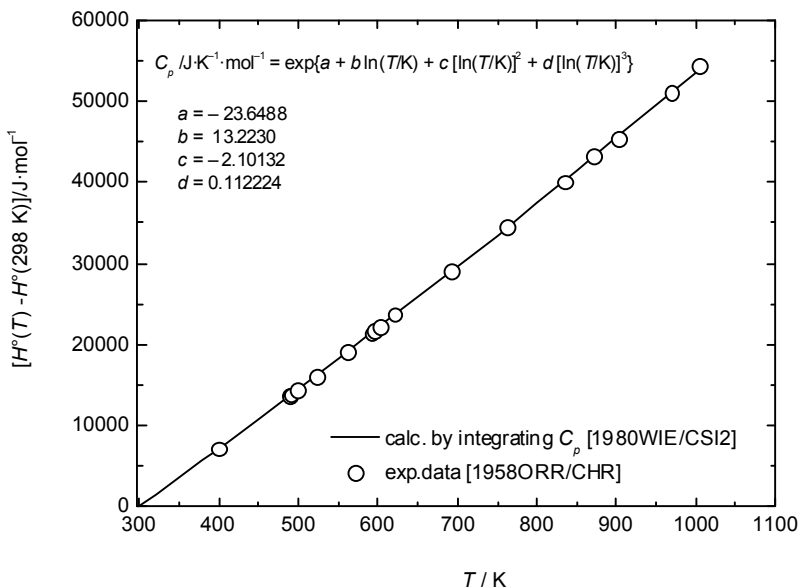
Tin(II) sulfide undergoes an isothermal phase transformation at 875 K, with a minor transition enthalpy  $\Delta_{\alpha}^{\beta}H = 669 \text{ J}\cdot\text{mol}^{-1}$ . The melting point of SnS was taken as  $T_{\text{fus}} = 1153 \text{ K}$  [1952ROS/WAG], the enthalpy of fusion was measured as  $\Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{SnS}, \beta) = 31.59 \text{ kJ}\cdot\text{mol}^{-1}$  and the corresponding entropy of fusion  $\Delta_{\text{fus}}^{\beta}H(\text{SnS}) = 27.40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The heat capacity of SnS(l) remains essentially constant over the 72 K-portion investigated, see Figure IX-1.

The enthalpy increments of Table A-14 are represented to within the average limits indicated by the equation below, see also Figure A-21.

SnS<sub>2</sub>(cr) (0.2%, 298-1000 K):

$$[H^\circ(T) - H^\circ(298.15 \text{ K})]/\text{kJ}\cdot\text{mol}^{-1} = 64.89 T/\text{K} + 8.79 \times 10^{-3}(T/\text{K})^2 - 20129.$$

Figure A-21: Enthalpy function of SnS<sub>2</sub>(cr).



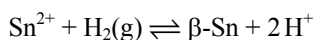
### [1958TOB]

In this paper the hydrolysis of Sn(II) has been studied by a potentiometric method using two sensors (glass and tin amalgam electrodes) at 25 °C and  $I = 3 \text{ M NaClO}_4$  ( $[\text{Sn}^{2+}]_{\text{tot}} = 2.5, 5, 10, 20$  and  $40 \text{ mM}$ ). The evaluation of the experimental data indicated the formation of  $\text{Sn}_3(\text{OH})_4^{2+}$  as the main product, while  $\text{Sn}_2(\text{OH})_2^{2+}$  and  $\text{Sn}(\text{OH})^+$  have been suggested as minor products.

This is a well documented and careful work. Since the composition of the minor hydrolysis products was later disputed [1964LIN/TU], [1976GOB], [1997SAL/FER], the combined data sets of [1958TOB] and [1976GOB] were re-evaluated for the purposes of this review. The combination of experimental data provides an excellent opportunity to determine the composition and formation constant of both mono- and oligonuclear complexes, since the total concentration of tin(II) varies in a very wide range ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.02$  to  $40.0 \text{ mM}$ ). The assumption of the presence of

two species ( $\text{Sn}_3(\text{OH})_4^{2+}$  and  $\text{Sn}(\text{OH})^+$ ) provides an excellent fit to the whole set of experimental data ( $\log_{10} \beta_{43}^* = -(6.75 \pm 0.01)$  ( $3\sigma$ ) and  $\log_{10} \beta_{11}^* = -(3.71 \pm 0.01)$ ). Including  $\text{Sn}_2(\text{OH})_2^{2+}$  into the equilibrium model, a slight (0.5%) decrease of the fitting parameter was obtained, but as its concentration never exceeds one percent of  $[\text{Sn}^{2+}]_{\text{tot}}$ , the formation of this species cannot be justified. The presence of  $\text{Sn}_2(\text{OH})_3^+$  (suggested by [1964LIN/TU]) was rejected by the computer program PSEQUAD [1991ZEK/NAG].

Apart from the importance for the hydrolysis of  $\text{Sn}^{2+}$ , this paper contains also potentiometric data for a  $\text{Sn}(\text{Hg})_{\text{sat}} | \text{Sn}^{2+} : \text{salt bridge} : \text{H}^+ | \text{H}_2(\text{g}) | \text{Pt}$  cell. Thus, once the activity of Sn in the  $\text{Sn}(\text{Hg})_{\text{sat}}$  phase is known, the standard potential of  $\text{Sn}^{2+}/\text{Sn}$  can be calculated. An attempt to extract from these data information on the standard electrode potential of reaction



failed, see Appendix A entry for [1967KRA].

### [1959ROB/STO]

In this classical textbook on electrolyte solutions the relationship between molality based  $\gamma_i$  and amount concentration based  $y_i$  activity coefficients has been derived most elegantly. In the light of this relationship the so far neglected Eq. (VI.5), connecting concentration and molality based standard electrode potentials, has been developed.

In addition activity coefficient data listed in this book enable in many cases to apply the SIT approach.

### [1960DON/MOS]

Anhydrous tin(II) sulfate was prepared by reaction of tin with  $\text{CuSO}_4$  in boiling water, evaporating most of the water, filtration of the crystals, washing with alcohol and ether and drying at 100 °C. Chemical analysis confirmed the formula.

“Clear solutions can be obtained at 20 °C provided that the concentration is greater than 18.9 g/100 mL”.

No details of the procedure and time of equilibration are given.

Table A-15: Solubility of tin sulfate at different temperatures.

$t/^\circ\text{C}$	20	30	50	60	100
Water	35.2	33.4	30.0	28.2	22.0
N- $\text{H}_2\text{SO}_4$ <sup>(a)</sup>	23.2	22.6	20.6	19.0	13.2
N- $\text{NaOH}$ <sup>(b)</sup>	2.27	2.29	2.52	2.62	-

(a) Probably 1.0 N  $\text{H}_2\text{SO}_4$ .

(b) Stannite expressed as g  $\text{SnSO}_4$ .

**[1960KLE/VAS]**

Results of investigations of the solubility of alpha- and beta-tin acid in nitric acid and sodium hydroxide solutions in absence and presence of NaF are reported for  $t = 20$  °C. Alpha-tin acid was prepared by reaction of tin with sulfuric acid and beta-tin acid by reaction with nitric acid. Precipitates were several times washed with distilled water.

Solubility in solutions of 0.01 – 1.0 M HNO<sub>3</sub> or NaOH and beta-tin acid in 0.05–0.5 M NaOH is such low that tin could not be detected by the applied indicator (hematoxylin, sensitivity  $\geq 5 \times 10^{-7}$  M). Solubilities of alpha-tin acid in solutions containing NaF and HNO<sub>3</sub> (pH = 1) at  $(20 \pm 0.1)$  °C:

NaF/M	0.05	0.1	0.2	0.3	0.4	0.5
Sn(IV)/M	0.0004	0.0010	0.0021	0.0032	0.0045	0.0055

No decrease of the total fluoride content in solution was observed, that means the solid did not absorb F<sup>-</sup>.

Since at pH = 1 fluoride is associated as HF(aq) the dissolution reaction below is assumed.



For the fluoro complex in solution  $K = \{\text{SnO(OH)}_{2-n}\text{F}_n(\text{aq})\}/\text{HF(aq)}^n$ , the total concentration of tin is approximately equal to the concentration of the fluoro complex. From a plot  $\log_{10}([\text{Sn(IV)}]) - \log_{10}([\text{NaF}])$  for the solubility data above  $n = 1$  was obtained. In absence of solid tin acid and excess of fluoride  $n$  increases. An equilibrium constant was derived using a dissociation constant  $K_{\text{HF(aq)}} = 1.16 \times 10^{-3}$  from the data above:

$$K = \{\text{SnO(OH)F(aq)}\}/\text{HF(aq)} = (1.05 \pm 0.09) \times 10^{-2}.$$

In addition a dissociation constant of the fluoro complex according to Reaction (A.35) of  $K = (5.3 \pm 0.2) \times 10^{-7}$  was calculated.



The chemical form of the fluorohydroxido complex (SnO(OH)F) is arbitrary, it could also be Sn(OH)<sub>3</sub>F or Sn(OH)<sub>3</sub>F(H<sub>2</sub>O)<sub>2</sub>.

The equilibrium constants are rough estimates, because control of ionic strength was not considered.

**[1961CON/PAU]**

Potentiometric measurements, using tin amalgam electrode, have been performed to study the formation of tin(II)-fluoride complexes in 0.5 and 2.0 M (Na,H)ClO<sub>4</sub> media at 298.15 K under nitrogen atmosphere ( $[\text{F}^-]_{\text{tot}} = 0.12$  to 0.24 M,  $[\text{Sn}]_{\text{tot}} = 0.004$  to

0.095 M,  $[F^-]_{\text{tot}}/[Sn]_{\text{tot}} = 1.4$  to 40). Only the formation of the  $SnF^+$  complex was considered by the authors. However, higher complexes ( $SnF_2(\text{aq})$ ,  $SnF_3^-$ ) may also form under the conditions used. Since no experimental data are provided, a re-evaluation is not possible. Besides, the authors noted the possible presence of tin(IV) during the measurements, and some discrepancies between the separate experiments. Therefore the reported data were not considered any further.

### [1961DON]

A crystalline material with an X-ray diffraction pattern identical with that of hydrous tin(II) oxide can be prepared by the hydrolysis of a basic tin(II) nitrate. Chemical analyses gave the formula  $5SnO \cdot 2H_2O$  (a cell content of  $Sn_{24}O_{14}(OH)_{20}$  is possible from lattice considerations). The composition  $24SnO \cdot 10H_2O$  could not easily be distinguished from  $5SnO \cdot 2H_2O$  by chemical analysis. The density calculated for the idealised formula is  $4.82 \text{ g} \cdot \text{cm}^{-3}$ , the density observed is  $(4.71 \pm 0.06) \text{ g} \cdot \text{cm}^{-3}$ .

### [1961DON/MOS]

The preparation of pure hydrous tin(II) oxide, tin(II) hydroxide has been investigated. The most probable composition is  $Sn_5O_3(OH)_4$ . Hydrous tin(II) oxide is dehydrated in one stage to give an orange amorphous material. This rapidly changes to blue-black tin(II) oxide on continued heating. The non-existence of the oxide  $Sn_3O_4$  in the disproportionation product of tin(II) oxide is proved.

The X-ray diffraction powder data for hydrous tin(II) oxide are given.

This would be a perfect starting material for a solubility study.

The formula accepted for tin(II) oxide hydroxide, hydroromarchite, is however  $Sn_6O_4(OH)_4$  [1996ABR/GRI].

### [1961DON/MOS2]

The preparation of a red modification of tin(II) oxide has been described and the exact conditions under which it can be obtained have been reported. The X-ray diffraction powder and unit-cell data of the material have been listed.

Red tin(II) oxide is stable in air up to about 570 K, possibly owing to the presence of a thin protective coating of tin(IV) oxide. The change from the red modification of tin(II) oxide to the blue-black form has been studied in a non-oxidising atmosphere by using high-temperature X-ray diffraction techniques; it was found that the change occurred at temperatures varying with the age of the sample.

Red tin(II) oxide can also be converted into the blue-black modification by mechanical pressure at room temperature, by treatment with strong alkali, or by contact with the stable modification, and must thus be considered metastable.

**[1961GOL/OGN]**

The formation of the thiocyanato complexes of tin(II) was studied by a potentiometric method using a tin amalgam electrode in aqueous solution as well as in methanol-water and acetone-water mixed solvents at 20 °C. In aqueous solution 2.2 M NaClO<sub>4</sub> was applied as inert electrolyte ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.0041 \text{ M}$ ) and the authors concluded the formation of three complexes ( $\text{SnSCN}_q^{2-q}$ ,  $q = 1, 2, 3$ ). The primary experimental data reported in the paper indicate that the background electrolyte was almost entirely replaced by NaSCN during the measurements. Due to the notable medium effect the experimental data were re-evaluated. Since the lowest thiocyanate concentration was 0.228 M, only four data points are available up to 30% replacement of the background electrolyte. The consideration of two species ( $\text{SnSCN}^+$  and  $\text{Sn}(\text{SCN})_2(\text{aq})$ ) is sufficient to describe the selected experimental data. The obtained formation constants are  $\log_{10} \beta_1 = (0.70 \pm 0.01)$  and  $\log_{10} \beta_2 = (1.65 \pm 0.01)$ . Considering the limited number of data points, an uncertainty of  $\pm 0.3$  has been assigned to the above values.

**[1961IVE/JAN]**

This is an exhaustive account with full bibliographies of the experimental methods by which the most reliable reference electrodes may be set up. The theoretical basis is treated comprehensively. Temperature and composition information is given for Calomel and Ag/AgCl electrodes, which is valuable throughout this review.

**[1961RAB/MOO]**

The authors re-evaluated the experimental data reported in [1950DUK/COU] and in [1952VAN/RHO]. The first set of data was satisfactorily fitted by three constants for the mono-, di- and trichlorido complexes (instead of the four constants given in [1950DUK/COU]). The recalculation of the data reported in [1952VAN/RHO] did not give consistent formation constants for the hydroxido complexes, therefore the presence of  $\text{Sn}(\text{OH})^+$  and  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$  under the given conditions has been rejected. The above conclusions are almost identical with those of the reviewers. Nevertheless, the recalculated formation constants reported in [1961RAB/MOO] are not used in the present assessment.

**[1961TOB/HUG]**

Potentiometric measurements using a tin amalgam electrode have been performed to study the complex formation processes between tin(II) and chloride ion under nitrogen atmosphere at 25 °C in 3 M (Na/H)ClO<sub>4</sub> medium. The formation constants of three mononuclear complexes ( $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$ ,  $\text{SnCl}_3^-$ ) have been reported. No evidence was found for polynuclear complexes involving chloride bridges. The careful measurements performed by the authors are similar to those reported in [1952VAN/RHO], but somewhat more extended range of hydrogen ion concentrations was used ( $[\text{H}^+]_{\text{tot}} = 0.05, 0.1$  and  $0.5 \text{ M}$ ). The graphical presentation of the experimental

data performed at different  $[H^+]_{\text{tot}}$  concentrations (Figure 1 in [1961TOB/HUG]) indicates no evidence for the formation of mixed chlorido-hydroxido complexes. During the measurements the chloride concentrations varied between 0 and 0.4 M. Considering the replacement of the  $\text{NaClO}_4$  by both  $\text{HClO}_4$  and  $\text{NaCl}$ , at most 30% of the background electrolyte was substituted during the measurements. Although no apparent medium effect was observed, an uncertainty of  $\pm 0.2$  has been assigned to the reported formation constants.

### [1962HAI/ZOL]

The solubility of  $(\text{CH}_3)_4\text{NSnCl}_3$  has been determined as function of the  $\text{HCl}$  concentration at 25 °C. In one experiment the ionic strength was varied (no background electrolyte was used), while in the second experiment a constant ionic strength of 4 M was applied using sulfuric acid as a 1:1 electrolyte. From the solubility curves the authors concluded the formation of four mononuclear chlorido complexes ( $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$ ,  $\text{SnCl}_3^-$  and  $\text{SnCl}_4^{2-}$ ) and calculated their formation constants. Due to the possible ion-pair formation between  $\text{Sn}^{2+}$  and  $\text{HSO}_4^-$  (see [1960GOR/BRU] and [1975WAD/ITO]) the sulfuric acid cannot be regarded as an inert electrolyte. In addition, the original ionic medium ( $\text{H}_2\text{SO}_4$ ) was entirely replaced by  $\text{HCl}$  during the measurements. The correct SIT treatment of the experimental data is not possible (only 12 experimental points are available and more than 20 parameters would be needed). Therefore, the reported formation constants for the  $\text{H}(\text{Cl}/\text{HSO}_4)$  medium were not considered further in this review. An attempt was made to use the solubility data obtained in  $\text{HCl}$  solutions to calculate the thermodynamic formation constants of the tin(II) chlorido complexes. However, the parameters ( $K_{s,0}^\circ$ ,  $\beta_q^\circ$  where  $q = 1$  to 4 and 5  $\Delta\epsilon$ ) are strongly correlated. Therefore, several sets of parameters describe the nine experimental data equally well. The authors themselves derived ‘semi-thermodynamic’ stability constants from these measurements, which can be defined as

$$^*K_q = \frac{[\text{SnCl}_q^{2-q}]}{[\text{SnCl}_{q-1}^{3-n}][\text{Cl}^-]\gamma_{\text{Cl}}}$$

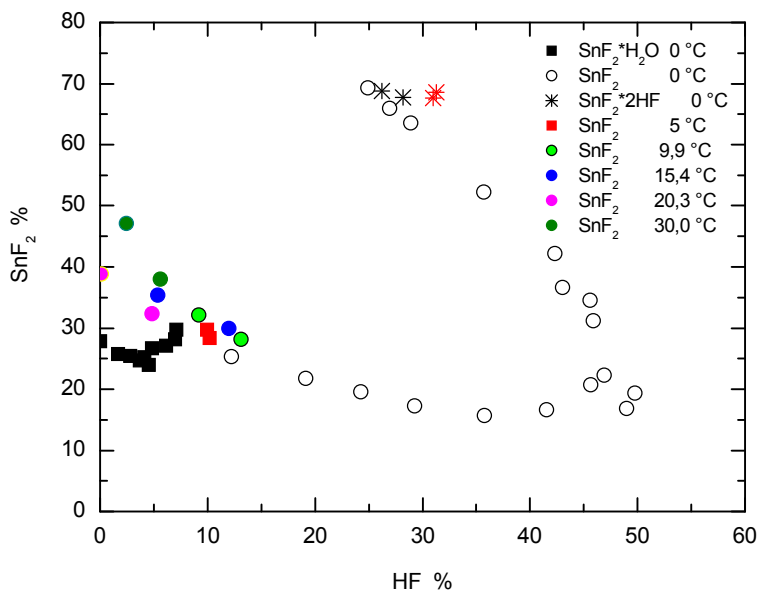
Since these constants are not compatible with the SIT, no thermodynamic data can be obtained from this paper.

### [1963BEA]

Solubility equilibria in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  had been determined at temperatures between 0 and 30 °C (see Figure A-22).

At  $t = 0$  °C a full isotherm has been determined (Table A-16). For solid phase composition Schreinemaker’s method was employed. For fluoride determination  $\text{HF}$  was distilled with 60%  $\text{HClO}_4$  at 135 °C. The distillate was then titrated with thorium nitrate and Alizarin Red as indicator. Unfortunately further experimental details are missing because the first 11 pages of the thesis were not available.

Figure A-22: Solubility isotherms in the system  $\text{SnF}_2\text{-HF-H}_2\text{O}$  in aqueous solutions at  $t = 0, 5, 9.9, 15.4, 20.3$  and  $30\text{ }^\circ\text{C}$ .



There are several solubility points, where the sum of  $\text{HF} + \text{SnF}_2$  exceeds 100% or is very near 100%. From the scatter of data an accuracy of 2 – 3% can be assumed. The composition of the solid phase for data above  $0\text{ }^\circ\text{C}$  seems to comply with anhydrous tin fluoride. Not all data were used, however, to determine the chemical composition of the wet residue. From the plot of all data a solubility of 40 – 50%  $\text{SnF}_2$  ( $4.5$  to  $9.0\text{ mol}\cdot\text{kg}^{-1}\text{ H}_2\text{O}$ ) at  $t = 25\text{ }^\circ\text{C}$  can be estimated. This is in agreement with the data of [1963HEF]. In a separate table the author reports “solubilities in water” at different temperatures without further remarks (Table A-18).

These data represent data from Table A-17 with the lowest HF content, however, still until 9%. In [1972GME] these data were listed as solubility in pure water. Using the complex formation constants selected by this review and  $\Delta_f G_m^\circ$  of  $\text{HF}(\text{aq})$ ,  $\text{HF}_2^-$  and  $\text{F}^-$  in Table IV-1 a Gibbs energy of formation  $\Delta_f G_m^\circ$  of  $\text{SnF}_2(\text{s})$  was estimated by stepwise simulation of solubility as shown in Figure A-23.



Table A-16: Solubility isotherm at  $t = 0$  °C.

100 $w(\text{HF})$ <sup>(a)</sup>	100 $w(\text{SnF}_2)$ <sup>(a)</sup>	$m_{\text{HF}}$ <sup>(b)</sup> /mol·kg <sup>-1</sup> H <sub>2</sub> O	$m_{\text{SnF}_2}$ <sup>(b)</sup> /mol·kg <sup>-1</sup> H <sub>2</sub> O	Solid
0	27.89	0.000	2.468	SnF <sub>2</sub> ·H <sub>2</sub> O
2.79	25.46	1.944	2.264	
3.7	24.73	2.584	2.205	
4.09	25.19	2.891	2.273	
4.53	23.95	3.166	2.137	
1.64	25.8	1.130	2.269	
4.84	26.7	3.534	2.489	
6.11	27.07	4.571	2.585	
6.99	28.21	5.392	2.778	
7.09	29.71	5.607	3.000	SnF <sub>2</sub> ·H <sub>2</sub> O
35.73	15.66	36.741	2.056	SnF <sub>2</sub>
29.23	17.28	27.315	2.061	
24.24	19.6	21.575	2.227	
19.11	21.74	16.149	2.345	
41.54	16.6	49.603	2.531	
12.19	25.34	9.754	2.588	
48.97	16.86	71.635	3.149	
45.67	20.73	67.941	3.937	
49.76	19.33	80.468	3.991	
46.91	22.35	76.278	4.640	
45.89	31.19	100.079	8.684	
45.61	34.51	114.679	11.077	
43	36.68	105.775	11.519	
42.32	42.15	136.212	17.320	
35.7	52.2	147.476	27.529	
28.88	63.61	192.219	54.050	
26.93	66.02	190.936	59.758	
24.93	69.36	218.236	77.515	SnF <sub>2</sub>
26.21	68.8	262.546	87.983	SnF <sub>2</sub> ·2HF
28.2	67.7	343.799	105.370	
30.97	67.66	1129.953	315.155	
31.3	68.63	22350.438	6256.452	SnF <sub>2</sub> ·2HF

(a) Original data.

(b) Calculated by this review.

Table A-17: Single solubility determination at various temperatures, solid phase: at  $t > 0$  °C probably SnF<sub>2</sub>.

$t/^\circ\text{C}$	100 $w(\text{HF})^{(a)}$	100 $w(\text{SnF}_2)^{(a)}$	$m_{\text{HF}}^{(b)}/\text{mol}\cdot\text{kg}^{-1} \text{H}_2\text{O}$	$m_{\text{SnF}_2}^{(b)}/\text{mol}\cdot\text{kg}^{-1} \text{H}_2\text{O}$
0	6.34	25.42	4.644	2.377
0	31.3	68.63	22350.438	6256.452
0	30.97	67.66	1129.953	315.155
0	26.21	68.8	262.546	87.983
5.1	10.17	28.42	8.278	2.953
5.1	31.77	69.11	-1804.572	-501.153
5.1	32.38	57.8	164.818	37.560
5.1	9.94	29.77	8.241	3.151
9.86	13.1	28.19	11.153	3.064
9.86	26.04	75.3	-971.350	-358.593
9.86	32.05	67.73	7281.906	1964.584
9.86	9.19	32.15	7.831	3.497
15.04	11.96	30	10.300	3.298
15.04	27.21	70.68	644.593	213.760
15.04	5.34	35.35	4.500	3.803
20.35	4.83	32.31	3.841	3.280
20.35	24.65	72.25	397.461	148.726
20.35	24.36	70.42	233.263	86.087
20.35	0.1	38.85	0.082	4.061
30	5.58	38.04	4.947	4.306
30	21.16	76.96	562.597	261.228
30	20.59	69.24	101.199	43.446
30	2.42	47.1	2.396	5.954

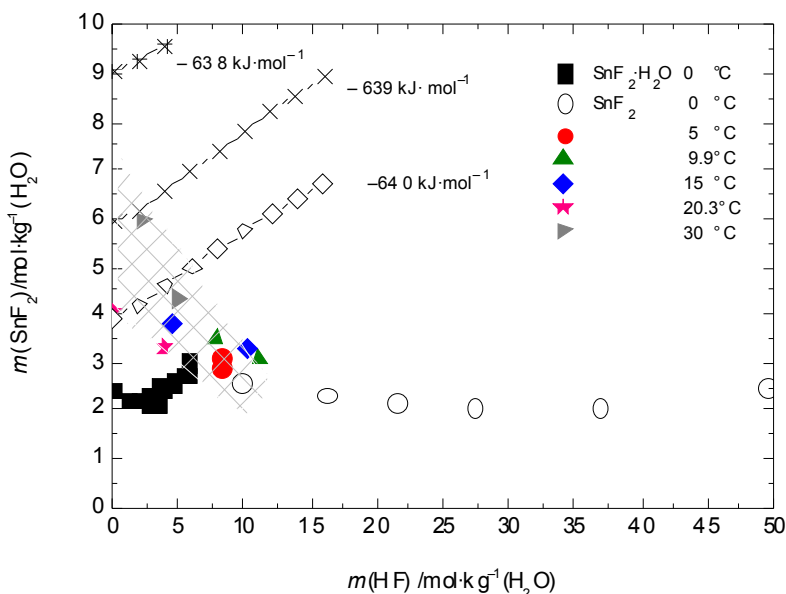
(a) Original data.

(b) Calculated by this review.

Table A-18: Solubility of Sn(II) fluoride in water.

$t/^\circ\text{C}$	100 $w(\text{SnF}_2)$	$m_{\text{SnF}_2}/\text{mol}\cdot\text{kg}^{-1} \text{H}_2\text{O}$
273.16	27.89	2.47
278.26	29.77	2.71
283.02	32.15	3.02
288.20	35.35	3.49
293.51	38.85	4.05
303.16	47.10	5.68

Figure A-23: Part of the diagram in Figure A-22. Solubility range for  $t = 5$  to  $30$  °C is shown by the shaded area. Line-symbol plot with  $-640$ ,  $-639$  and  $-638$   $\text{kJ}\cdot\text{mol}^{-1}$  represent simulation results with the assumed  $\Delta_f G_m^\circ$  of  $\text{SnF}_2(\text{s})$ .



Values between  $-640$   $\text{kJ}\cdot\text{mol}^{-1}$  to  $-638$   $\text{kJ}\cdot\text{mol}^{-1}$  cover the experimental data area. Since the simulation results depend on the formation constants  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  of the fluoridocomplexes the sensitivity of the simulated solubilities was tested. Changing  $\beta_1$  and  $\beta_2$  by one order of magnitude and  $\beta_3$  by three orders of magnitude, all in the direction to higher values enhanced the solubility from  $4.0$   $\text{mol}\cdot\text{kg}^{-1}$   $\text{H}_2\text{O}$  to  $8.9$   $\text{mol}\cdot\text{kg}^{-1}$   $\text{H}_2\text{O}$ . This is still well within the range of experimental uncertainty. Thus it is concluded that  $-(639.0 \pm 1.0)$   $\text{kJ}\cdot\text{mol}^{-1}$  can be accepted as a first estimate of  $\Delta_f G_m^\circ$  for  $\text{SnF}_2(\text{s})$ .

### [1963DON/MOS]

Of the various tin(II) chlorides reported in the literature, the only one producible as a clearly defined crystalline phase from aqueous solution was found to be  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ . The pure material was obtained from solutions of pH ranging from 1.14 to 4.50.

X-ray diffraction data given show that the crystals of  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$  are orthorhombic with unit cell dimensions:  $a = 10.18$  Å,  $b = 17.06$  Å,  $c = 14.66$  Å, and eight formula-units per cell.

$\text{Sn}_4\text{Cl}_2(\text{OH})_6$  is structurally identical with single crystals investigated by [1981SCH/NES], although the composition of the latter was found to be

$\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ , which is the at present accepted formula of basic tin(II) chloride, abhurite.

### [1963HEF]

The author summarised properties of  $\text{SnF}_2$  from literature. A solubility plot from “Tech. Data Sheet No. 142, M & T Chemicals, Inc., March 1961.

The temperature dependence of the solubility is described as to be linear.

Plots are given for the effect of aging of 0.4%  $\text{SnF}_2$  solutions at different pH from 3.0 to 4.5. The concentration of  $\text{Sn}^{2+}$  decreases to 90% of the initial concentration at pH = 3.0 during the first 20 days and remains constant until 100 days, the maximum time of observation. At pH = 4.5 the decrease of  $\text{Sn}^{2+}$  concentration reaches 50% after 100 days and is still further decreasing. Solutions of  $\text{SnF}_2$  are more stable than those of  $\text{SnCl}_2$ .

### [1964DON/DON]

The authors prepared the solid compounds:  $\text{MSnF}_3$  and  $\text{MSn}_2\text{F}_5$  with  $\text{M} = \text{NH}_4, \text{Na}, \text{K}$  by adding the fluoride  $\text{MF}$  to a solution of  $\text{SnF}_2$ . Compounds were analyzed for tin(II), total tin and fluoride. At least at 60 °C the trifluorostannates dissolve incongruently under crystallisation of the  $\text{Sn}_2\text{F}_5^-$  salt. Solubility data are given in g/100 mL solution without densities. The compound  $\text{MSnF}_3$  is obviously much more soluble than  $\text{MSn}_2\text{F}_5$ . The analytical error in solubility determination given by the authors is 1% absolute. The authors performed potentiometric measurements, too, and reported the existence of a dinuclear  $\text{Sn}_2\text{F}_5^-$  ion when concentrated aqueous solutions of  $\text{SnF}_2$  ( $[\text{Sn}^{2+}] > 0.3 \text{ M}$ ) were titrated by  $\text{MF}$  solutions.

X-ray powder diffraction data for these compounds are reported and unit cell parameters were determined from the compounds.

Table A-19: Solubility of the compounds  $\text{MSnF}_3$  and  $\text{MSn}_2\text{F}_5$  ( $\text{M} = \text{NH}_4, \text{Na}, \text{K}$ ) in  $\text{H}_2\text{O}$  and 0.1 M HF at different temperatures.

	Solubility/(g/100 mL solution)					
	Pure water			1 M HF		
	25 °C	40 °C	60 °C	25 °C	40 °C	60 °C
$\text{NH}_4\text{SnF}_3$	59	74	78	59	65	79
$\text{NH}_4\text{Sn}_2\text{F}_5$	4.4	6.4	10.6	8.6	9.3	10.5
$\text{Na}_3\text{SnF}_3$	9.6	26.6	Incongr.	13.5	15.2	Incongr.
$\text{NaSn}_2\text{F}_5$	5.6	8.4	11.7	6.0	8.1	10.4
$\text{KSnF}_3$	9.1	13.7	Incongr.	11.4	12.8	Incongr.
$\text{KSn}_2\text{F}_5$	2.5	6.8	12.3	5.1	6.9	9.9

**[1964GEY/MUC]**

The solubility of SnS was determined by shaking about 0.6 g SnS in 300 mL of 0.1 M and 1.0 M HCl solution under a CO<sub>2</sub> atmosphere in a closed glass vessel. After 4 h (selected after testing time dependence of results) a solution sample was taken and injected into 25 mL 20% HCl, which was boiled and purged with CO<sub>2</sub> before to remove dissolved air. Then the acid solution was boiled under a CO<sub>2</sub> stream for 20 min to remove H<sub>2</sub>S. Then the tin was determined iodometrically by the method of Höltje with a 0.01 M iodine solution.

SnS dissolves completely in 3 – 4 M HCl and 2 M NaOH. The results at 20 °C are given in Table A-20.

Table A-20: Solubility of SnS in HCl at 20 °C.

[HCl]/M	SnS SOL./mL	Titrated 0.01 M I <sub>2</sub> /M	Sn found/mg	Solubility SnS/M
0.1	50	0.39	0.23	$3.9 \times 10^{-5}$
0.1	50	0.40	0.24	$4.0 \times 10^{-5}$
0.1	50	0.40	0.24	$4.0 \times 10^{-5}$
1.0	20	1.09	0.647	$2.7 \times 10^{-4}$
1.0	20	1.04	0.617	$2.6 \times 10^{-4}$
1.0	20	0.95	0.563	$2.4 \times 10^{-4}$

In parallel determinations the authors checked for absence of tin(IV) by treating the solution with iron before titration.

No explicit information about temperature constancy is given,  $\Delta T = \pm 2$  K should be assumed.

Tin(II) sulfide used for the solubility experiments was carefully under exclusion of air. Tin was dissolved in boiled HCl solution and SnS precipitated by air-free H<sub>2</sub>S. Chemical analysis yielded an atomic ratio S/Sn = 1.000.

**[1964YOU/GIL]**

Several Pt-metal salts react with Sn(II) chloride leading to complex anions with compositions of  $[\text{RuCl}_2(\text{SnCl}_3)_2]^{2-}$ ,  $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ ,  $[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]^{4-}$  and *cis/trans*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ , where the trichlorostannate(II) ion is considered to be acting as an anionic ligand with donor strength comparable to chloride ion. Neutral complexes of Rh, Ir, and Pt were also prepared in which diolefin, triphenyl-phosphine/arsine ligands are also coordinated to the metal ion beside a  $\text{SnCl}_3^-$  group (e.g.  $(\text{C}_7\text{H}_8)_2\text{RhSnCl}_3$  and  $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$ ).

**[1965HAA/DUC]**

Haase *et al.* carried out partial vapour pressure and isopiestic measurements on aqueous solutions of nitric and perchloric acid. The activity coefficients of HNO<sub>3</sub>-H<sub>2</sub>O solutions were reported in the range of 2 to 28 mol·kg<sup>-1</sup> at 25, 50 and 75 °C. The activity coefficients of HClO<sub>4</sub>-H<sub>2</sub>O solutions were reported in the range of 0.1 to 13 mol·kg<sup>-1</sup> at 10 and 40 °C and in the range of 0.1 to 16 mol·kg<sup>-1</sup> at 75 °C, respectively.

An SIT analysis of their results on HClO<sub>4</sub>-H<sub>2</sub>O was carried out, according to the recommendation given in Appendix B. This analysis is summarised in Figure A-24 and Figure A-25. Between 10 ≤ *t*/°C ≤ 40 the ion interaction coefficient,  $\epsilon(\text{H}^+, \text{ClO}_4^-)$ , is, within the experimental error limits, independent of temperature and agrees quite well with the value given in Table B-4.

Figure A-24: Activity coefficients of HClO<sub>4</sub> at different temperatures ( $\Delta$ : data at 10 °C [1965HAA/DUC];  $\circ$ : data at 25 °C [1959ROB/STO];  $\nabla$ : data at 40 °C [1965HAA/DUC]; solid line: prediction,  $\alpha(\text{H}^+, \text{ClO}_4^-) = 0.14 \text{ kg}\cdot\text{mol}^{-1}$  (see Table B-4 [2005GAM/BUG]); dashed line: prediction,  $\alpha(\text{H}^+, \text{ClO}_4^-) = 0.147 \text{ kg}\cdot\text{mol}^{-1}$  (SIT analysis of [1965HAA/DUC]).

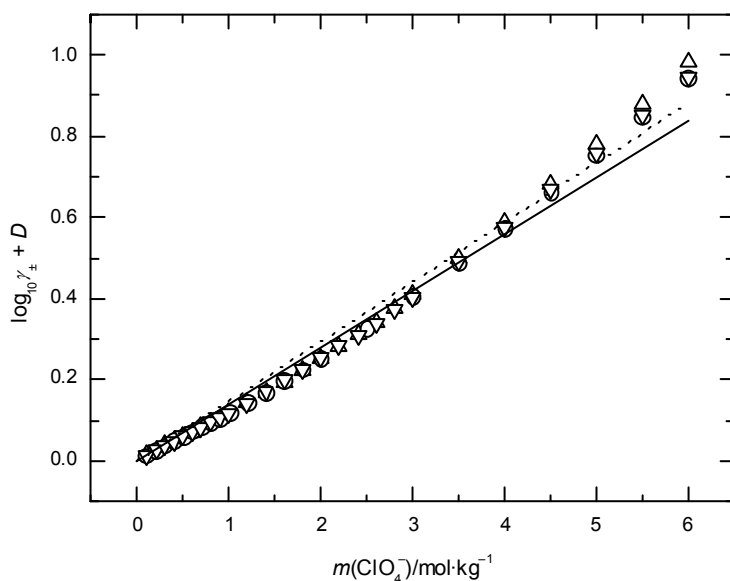
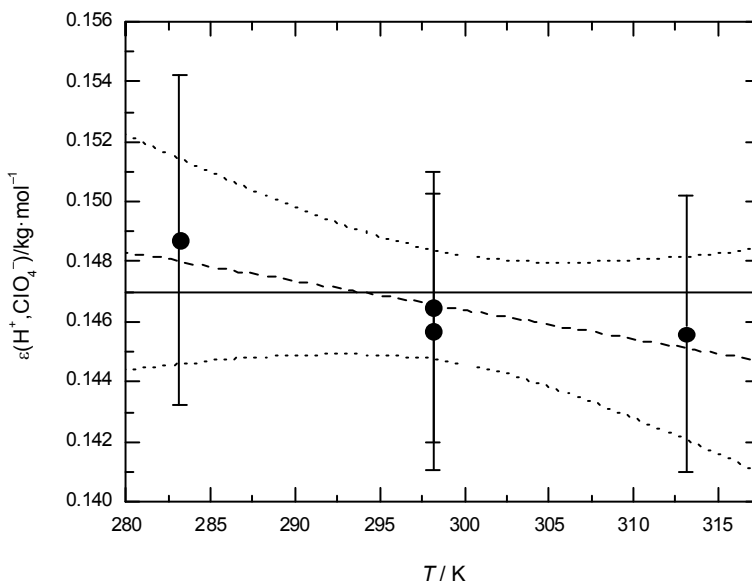
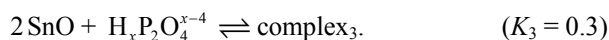
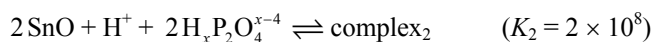
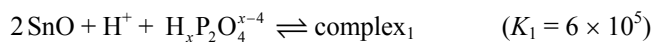


Figure A-25: Temperature dependence of  $\varepsilon(\text{H}^+, \text{ClO}_4^-)$  (●: data from linear regressions; solid line:  $\partial\varepsilon/\partial T = 0$ ,  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.147 \text{ kg}\cdot\text{mol}^{-1}$ ; dashed line: linear fit  $\partial\varepsilon/\partial T = -(0.97 \pm 4.7) \times 10^{-4} \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ; dotted lines: 95% confidence limits).



### [1966MES/IRA]

The stability of tin(II)-pyrophosphate and -tripolyphosphate complexes has been determined by equilibrating the polyphosphate solutions with solid SnO. The measurements were performed between pH 5 to 7, at 25 °C and in 1 M NaClO<sub>4</sub> solution under nitrogen atmosphere. High purity SnO (Baker and Adamson) was used, but further characterisation is not provided. The dissolved tin(II) was determined iodometrically. The equilibration of the two phases lasted 24 hours. Sodium complexes of pyrophosphate were not taken into account in the calculations. The solubility of SnO showed a maximum around pH 5. The pyrophosphate proved to be a strong complex forming ligand, since the concentration of the dissolved tin(II) exceeded the concentration of pyrophosphate in solution with  $[\text{P}_2\text{O}_7^{4-}]_{\text{T}} = 0.005$  or 0.015 M, therefore the authors suggested the formation of polynuclear complexes. The whole set of data was explained by the following three reactions and equilibrium constants



Since the protonation state and the correct composition of the complexes was not determined, the reported equilibrium data were not considered in this review.

The solubility of SnO(s) in dilute HClO<sub>4</sub> solutions maintained at  $I = 1.0$  M with NaClO<sub>4</sub> was also studied at 25 °C. From these data a constant for the hydrolysis reaction was obtained



High purity SnO supplied by Baker and Adamson was used throughout.

The data, listed in Table 1 of this work, provide probably the most reliable information (pH, [Sn(II)]<sub>tot</sub>,  $I = 1$  M NaClO<sub>4</sub>) available for the determination of  $\log_{10} {}^*K_{s,0}^o$  for reaction



Although no structural information on the SnO(s) used for this solubility study has been given, a detailed re-analysis of [1966MES/IRA] revealed that only the solubility constant according to Eq. (A.36) can be derived reliably from the experimental data pH,  $m_{\text{Sn(II)}}$ . Under the prevailing conditions SnOH<sup>+</sup> and Sn<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> contribute 5 to 12% to  $m_{\text{Sn(II)}}$ , whereas Sn(OH)<sub>2</sub>(aq) is completely negligible. Consequently the determination of  ${}^*K_{s,0}^o$  (A.36) was based on Eq. (A.37)

$$m_{\text{Sn(II)}}/a_{\text{H}^+} = {}^*K'_{s,1} + ({}^*K'_{s,0} + 3{}^*K'_{s,43})a_{\text{H}^+}. \quad (\text{A.37})$$

${}^*K'_{s,0}$ ,  ${}^*K'_{s,1}$  and  ${}^*K'_{s,43}$  are “mixed” constants, where H<sup>+</sup> is expressed as activity but all other reacting species are expressed as molalities. The actual regression analysis was carried out in such a way that  ${}^*K_{s,1}^o$  and  ${}^*K_{s,43}^o$  were selected from the TDB Sn Review, and were transformed to  ${}^*K'_{s,1}$  and  ${}^*K'_{s,43}$  employing the SIT formalism. The latter constants as well as  ${}^*K'_{s,0}$  depend on  $\Delta_f G_m^o$  (SnO, cr, 298.15 K), so the final values of these quantities were arrived at iteratively. As SnOH<sup>+</sup> and Sn<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> contributed less than 12% to the total solubility convergence was achieved after a few iterations. The result of this recalculation is summarised in Figure A-26. As soon as  ${}^*K_{s,1}^o$  and  ${}^*K_{s,43}^o$  are known  $\log_{10} K_{s,0}^o$  can alternatively be determined by regression analysis of  $\log_{10} m_{\text{Sn}^{2+}}$  vs. pH data, see Figure VII-9.

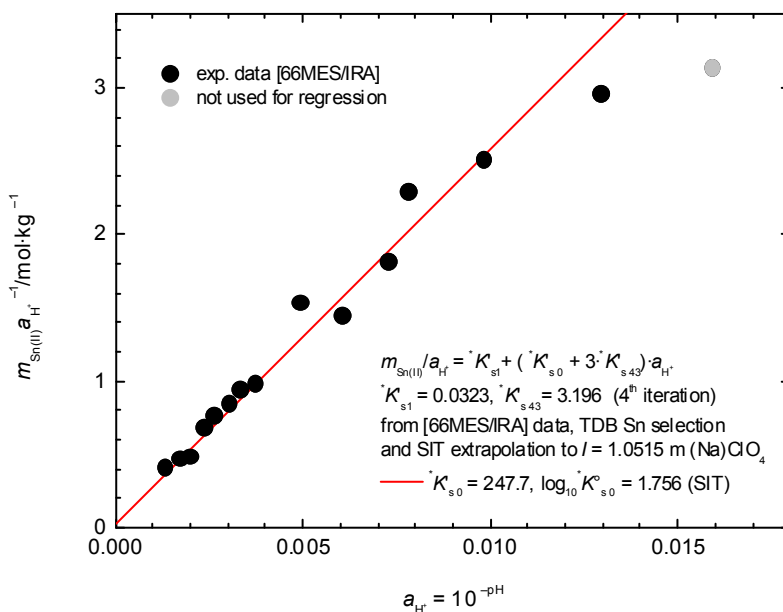
### [1966VAS/LOB]

A calorimeter for measuring thermal effects in solution has been described. The temperature sensor is a differential thermo-battery of 280 copper / Constantan thermocouples. The temperature was recorded by an automatic electronic potentiometer on a ribbon diagram. The sensitivity of the calorimeter is  $6 \times 10^{-5}$  K in temperature and  $1.0 \times 10^{-3}$  J in heat. The mean error in determining the thermal effects does not exceed 0.25%.



This precision calorimeter was tested by measuring the heat of dissolution of KCl at 18, 25, 35, 40, 55, 70, and 85 °C [1966VAS/LOB2]. The result agreed with the generally accepted value.

Figure A-26: Solubility of SnO(cr) in 1.050 M NaClO<sub>4</sub> solutions at 25 °C (●: experimental data; solid line: iterative linear regression analysis).



### [1966VAS/LOB2]

To test the operation of a precision calorimeter [1966VAS/LOB] the heat of dissolution of KCl at a dilution of 1:450 was measured at 18, 25, 35, 40, 55, 70, and 85 °C. It was demonstrated that the precision calorimeter described in [1966VAS/LOB] operates very well.

### [1967DAV/DON]

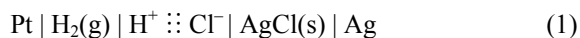
Solutions of sodium hydroxide were added to solutions of tin(II) sulfate under air-free conditions. Pure tritin(II) dihydroxide oxide sulfate, Sn<sub>3</sub>(OH)<sub>2</sub>OSO<sub>4</sub>, was obtained from solutions of pH 1.5 to 2.4. Above pH 2.4 two distinct phases were identified in the precipitate, basic tin(II) sulfate and hydrous tin(II) oxide.

A single crystal X-ray study resulted in the following crystal data for basic tin(II) sulfate, Sn<sub>3</sub>(OH)<sub>2</sub>OSO<sub>4</sub>: orthorhombic,  $a = (4.970 \pm 0.005) \text{ \AA}$ ,  $b =$

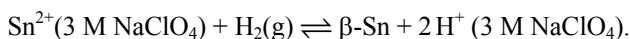
$(13.15 \pm 0.01) \text{ \AA}$ ,  $c = (12.21 \pm 0.01) \text{ \AA}$ ,  $V_{\text{cell}} = 798 \text{ \AA}^3$ ,  $Z = 4$ ,  $d(\text{obsd}) = 4.12 \text{ g}\cdot\text{cm}^{-3}$ ,  $d(\text{X-ray}) = 4.18 \text{ g}\cdot\text{cm}^{-3}$ . Space group *Pbcm* or *Pca2*<sub>1</sub>.

### [1967KRA]

For the determination of the standard potentials of  $\text{Cd}^{2+}/\text{Cd}$ ,  $\text{Tl}^+/\text{Tl}$ ,  $\text{Ag}^+/\text{Ag}$ ,  $\text{AgCl}/\text{Ag}$ , and of the quinhydrone electrode potential measurements were performed at  $25 \text{ }^\circ\text{C}$  and  $I = 1.0, 2.0, 3.0 \text{ M}$  ( $\text{NaClO}_4$ ) using the cells



The experimental data collected with cell (1) can possibly be combined with measurements of [1958TOB] and [1976GOB] to determine  $E^\circ$  for the reaction



Recalculation led to the results given in Table A-21 for the following reaction at  $298.15 \text{ K}$ :

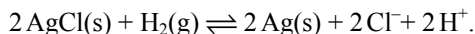


Table A-21: Standard potential of the reaction  $2 \text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightleftharpoons 2 \text{Ag}(\text{s}) + 2 \text{Cl}^- + 2 \text{H}^+$  recalculated by combining the data of cell (1) with the measurements of [1958TOB] and [1976GOB].

$E^\circ / \text{mV}$	$I / \text{mol}\cdot\text{dm}^{-3}$
$232.27 \pm 0.22$	1.0 ( $\text{NaClO}_4$ )
$220.33 \pm 0.42$	2.0 ( $\text{NaClO}_4$ )
$203.48 \pm 0.81$	3.0 ( $\text{NaClO}_4$ )

### [1967KWE/VRO]

The preparation of spectrochemically pure, tetragonal black tin(II) oxide is described. Orthorhombic red tin(II) oxide can also be obtained with the same purity grade, apart from 1% P contamination, due to the stabilisation with  $\text{PO}_4^{3-}$  ions. A very pure red tin(II) oxide with unknown structure was prepared without stabiliser by a special precipitation procedure. The X-ray diagram of the latter phase was not identical with the diagram of red  $\text{SnO}$  stabilised by  $\text{PO}_4^{3-}$  ions.

Thermodynamic investigations of tin(II) oxides should start with samples prepared by the procedures described in this paper.

**[1967LAW]**

A series of isothermal experiments was carried out in which dry SnO was heated in an atmosphere of nitrogen free from oxygen for times varying from 15 min to 16 h at 700-1050 K. The resultant disproportionation products were analyzed nondestructively by the use of electron diffraction, X-ray diffraction, and Mössbauer spectroscopy. Electron micrographs were prepared to enable phase identifications to be made. Besides metallic Sn and SnO<sub>2</sub>, a new phase was evident in those samples which were heated for short times or at low temperatures. This material was always in the form of thin single crystal platelets measuring 1000 Å<sup>2</sup> × 50 Å. X-ray and electron diffraction analyses showed that the crystal habit of the platelet was triclinic with  $a = (4.86 \pm 0.16)$ ,  $b = (5.88 \pm 0.14)$ ,  $c = (8.20 \pm 0.17)$  Å,  $\alpha = (93^\circ 00' \pm 0.17')$ ,  $\beta = (93^\circ 21' \pm 21')$ ,  $\gamma = (91^\circ \pm 24')$ . The principal X-ray diffraction lines for the new phase are given. From considerations of the theoretical density of a crystal with the dimensions as given, and of the transformation mechanism necessary to convert SnO to the intermediate material, the most probable composition of the new phase is Sn<sub>3</sub>O<sub>4</sub>. Mössbauer spectra obtained by using a <sup>119</sup>Sn source were not inconsistent with a formula Sn<sub>2</sub><sup>II</sup>Sn<sup>IV</sup>O<sub>4</sub> for the phase. The metastable material decomposes on further heating into β-Sn and SnO<sub>2</sub>. The kinetics of the decomposition are 1<sup>st</sup> order with respect to the intermediate oxide.

**[1967VAS]**

The calculation of standard heats of reaction in electrolyte solutions has been examined. For the calculation of standard enthalpies the relative apparent and partial molar enthalpies of solute and solvent have to be taken into account.

The dependence on ionic strength of the heat of reaction can be approximately described by an equation based on Debye-Hückel formulae. The equation

$$\Delta H - \Delta z^2 \left[ \frac{235.9 \cdot I^{0.5}}{1 + 1.6 \cdot I^{0.5}} - \frac{149.0 \cdot I}{(1 + 1.6 \cdot I^{0.5})^2} \right] = \Delta H^\circ + i \cdot I$$

has been proposed for extrapolation of  $\Delta_r H_m$  to  $\Delta_r H_m^\circ$ . This formula has been used by many scientists particularly in Russia. It should be emphasised that [1998PLY/GRE] criticised Vasil'ev's extrapolation to  $I \rightarrow 0$  on the basis of thermodynamic considerations ([1997ALL/BAN], p 414). A controversy ensued, see [1978VAS/YAS], [1996PLY/GRE], [1997VAS] and [1998PLY/GRE]. Although only minor errors may be introduced by Vasil'ev's approach, it has been decided that in this review respective evaluations should be based on the thermodynamically correct SIT method, see [1997ALL/BAN], p 412.

**[1967VAS/LOB]**

The heat of ionisation of water has been measured calorimetrically between 0 and 70 °C and  $0.04 \leq I/M \leq 3.0$  (NaNO<sub>3</sub>). At constant ionic strength,  $I$ , the heat of ionisation decreases with  $T$ . At constant  $T$  the heat of ionisation increases with ionic strength at high  $T$  and decreases at low  $T$ .

The equation:

$$\Delta H - \Delta z^2 \left[ \frac{\alpha \cdot I^{0.5}}{1 + \beta \cdot I^{0.5}} - \frac{\gamma \cdot I}{(1 + \beta \cdot I^{0.5})^2} \right] = \Delta H^{\circ} + i \cdot I$$

proposed by [1967VAS] for calculation of the standard heat change from direct calorimetric data has been found to apply at all temperatures investigated.

Coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are given for 0 to 70 °C (Table 3.)

While this paper summarises data needed for a recalculation of the results of Vasil'ev and coworkers it should be emphasised that [1998PLY/GRE] criticise Vasil'ev's extrapolation to  $I \rightarrow 0$  on the basis of thermodynamic considerations ([1997ALL/BAN], p 414).

**[1968BOT/CIA]**

The interaction of copper(II) with pyrophosphate ion have been studied by potentiometry. The authors reported reliable dissociation constants of pyrophosphoric acid in 3 M NaClO<sub>4</sub>.

**[1968CIL]**

The solubility of SnHPO<sub>4</sub>·0.5H<sub>2</sub>O and the formation of phosphato complexes of tin(II) have been studied by solubility measurements in 0.2 M NaClO<sub>4</sub> solutions at 25 °C. The pH of the solutions was kept constant at pH = 2.48. The solid SnHPO<sub>4</sub>·0.5H<sub>2</sub>O was prepared by the author and was identified as the  $\beta$ -phase by X-ray powder diffraction. The total concentration of tin(II) was determined by colorimetric analysis using 1,5-diphenylcarbohydrazide. The author mentioned, that measurements at a constant pH give no information on the protonation state of the coordinated ligand(s). Nevertheless, he explained the data by assuming the equilibrium  $\text{SnHPO}_4 \cdot 0.5\text{H}_2\text{O} \rightleftharpoons \text{Sn}^{2+} + \text{HPO}_4^{2-} + 0.5\text{H}_2\text{O}$  ( $\log_{10} K_{s,0} = -12.82$ ),  $\text{Sn}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{SnHPO}_4(\text{aq})$  ( $\log_{10} \beta_1 = 7.83$ ) and  $\text{Sn}^{2+} + 3\text{HPO}_4^{2-} \rightleftharpoons \text{Sn}(\text{HPO}_4)_3^{4-}$  ( $\log_{10} \beta_3 = 10.04$ ). The author used  $\text{p}K_1 = 2.10$ ,  $\text{p}K_2 = 7.19$  and  $\text{p}K_3 = 12.38$  for the dissociation constants of phosphoric acid. These values are correct at infinite dilution, but considerably different constants are valid in 0.2 M NaClO<sub>4</sub> solution ( $\text{p}K_1 = 1.87$ ,  $\text{p}K_2 = 6.65$  and  $\text{p}K_3 = 11.52$ ). Using the equilibrium constants reported in [2000CIA/IUL2], under the conditions used in [1968CIL] the formation of  $\text{SnH}_2\text{PO}_4^+$ ,  $\text{Sn}(\text{H}_2\text{PO}_4)(\text{HPO}_4)^-$ ,  $\text{SnHPO}_4(\text{aq})$  can be expected. Therefore, the primary data reported in [1968CIL] can only be used to determine the solubility

constant of  $\text{SnHPO}_4 \cdot 0.5\text{H}_2\text{O}$ . Using the data for low phosphate concentration (0.3 to 2.5 mM)  $\log_{10} K_{s,0} = -(12.21 \pm 0.05)$  can be calculated.

### [1968DEA/EVA]

Approximately 100 anions of the general type  $[\text{SnF}_{6-n}\text{X}_n]^{2-}$  have been characterised in different solvents by  $^{19}\text{F}$  NMR spectroscopy, where X is one of a wide range of unidentate ligands or half a bidentate ligand. Besides the reported  $^{19}\text{F}$  chemical shifts, Sn–F and F–F coupling constants, *cis-trans* ratios have been obtained for many of the geometrical isomers. Equilibrium constants for the reactions  $\text{SnF}_5(\text{H}_2\text{O})^- + \text{F}^- \rightleftharpoons \text{SnF}_6^{2-}$  and  $\text{SnF}_6^{2-} + \text{X}^- \rightleftharpoons \text{SnF}_5\text{X}^{2-} + \text{F}^-$  (where  $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{OH}^-$ ) have been determined at  $(20 \pm 2)^\circ\text{C}$ . The equilibrium constant for the formation of chlorido-fluorido and bromido-fluorido mixed complexes were determined in solutions 1.2 M  $(\text{NH}_4)_2\text{SnF}_6 + 3 \text{ M } (\text{H}_3\text{NH}_4)\text{X}$  (where  $\text{X} = \text{Cl}, \text{Br}$ ). The background electrolyte used for studying the reaction  $\text{SnF}_6^{2-} + \text{OH}^- \rightleftharpoons \text{SnF}_5\text{OH}^{2-} + \text{F}^-$  is uncertain.

Since the ligand exchange between the different species is slow on the NMR time scale, the formation of mixed complexes were directly observed, proving their existence. Nevertheless, the reported equilibrium data cannot be used to derive selected values: (i) the constants determined at high ionic strength cannot be extrapolated to zero ionic strength, (ii) several experimental details are uncertain or doubtful (*e.g.* for the determination of the equilibrium constants of the mixed hydroxido complex, the authors used  $\text{p}K_w = 14.19$ , suggesting that relatively high ionic strength was applied, but background electrolytes were not reported).

### [1968HAI/JOH]

The complex formation between Sn(II) and iodide was studied by measuring the solubility of  $\text{SnI}_2(\text{s})$  and  $[\text{Me}_4\text{N}]_2\text{SnI}_4(\text{s})$  at  $25^\circ\text{C}$  in a 4.0 M  $\text{NaClO}_4$  medium. The authors suggested the formation of six mononuclear complexes  $\text{SnI}_q^{2-q}$ , with  $q = 1, 2, 3, 4, 6,$  and  $8$ . It was shown that no ion pair formation takes place between  $\text{Me}_4\text{N}^+$  and  $\text{I}^-$  or between  $\text{Me}_4\text{N}^+$  and  $\text{SnI}_q^{2-q}$ . The authors used two different ranges of iodide concentrations. The solubility of  $\text{SnI}_2(\text{s})$  and  $[\text{Me}_4\text{N}]_2\text{SnI}_4(\text{s})$  were determined for  $[\text{I}^-]_{\text{ini}} = 0$  to 1.0 M and  $[\text{I}^-]_{\text{ini}} = 0.5$  to 3.99 M, respectively. It means, that the original background electrolyte ( $\text{NaClO}_4$ ) was entirely replaced by  $\text{NaI}$  during the solubility measurements of  $[\text{Me}_4\text{N}]_2\text{SnI}_4(\text{s})$ . Therefore, the experimental data were re-evaluated for the purposes of this review, using only the solubility data obtained for  $\text{SnI}_2(\text{s})$ . Up to  $[\text{I}^-]_{\text{ini}} = 0.6 \text{ M}$  (15% replacement of the background electrolyte) the presence of four species ( $\text{SnI}_q^{2-q}$ ,  $q = 1, 2, 3, 4$ ) is sufficient to describe the experimental data. The recalculated constants are as follows:  $\log_{10} K_{s,0}(\text{SnI}_2) = -(5.08 \pm 0.10)$ ,  $\log_{10} \beta_1 = (0.75 \pm 0.30)$ ,  $\log_{10} \beta_2 = (1.14 \pm 0.30)$ ,  $\log_{10} \beta_3 = (1.60 \pm 0.30)$ ,  $\log_{10} \beta_4 = (2.69 \pm 0.30)$  (the uncertainties are estimated by the reviewers). It should be noted, that the consideration of at least one additional complex (*e.g.*  $\text{SnI}_5^{3-}$ ) is necessary to fit the

solubility data up to  $[I^-]_{ini} = 1.0 \text{ M}$ , therefore further studies are required to establish the composition and stability of the formed complexes at higher iodide concentrations.

### [1968HAL/SLA]

The formation constants for the fluoride complexes of Sn(II) were determined by potentiometric measurements by using both tin amalgam and fluoride ion selective electrodes under nitrogen atmosphere. The experiments were performed using constant tin(II) concentration at ionic strength of 0.85 M and at three different temperatures ( $t = 25, 45$  and  $60 \text{ }^\circ\text{C}$ ). The background electrolyte used in this study is ambiguous. Although, no information is provided about the inert electrolyte (0.85 M) used for the measurements, the calibration of the fluoride selective electrode was made in 0.1 and 1.0 M perchlorate media, thus 0.85 M  $\text{NaClO}_4$  was presumably the background electrolyte. Some further experimental details (concentration of  $[\text{Sn}^{2+}]_{tot}$  and  $[\text{H}^+]_{tot}$  in the solutions) were not reported in [1968HAL/SLA], too. Taking into account the fact that  $([\text{F}^-]_{tot} - [\text{F}^-]_{free})/3$  should be nearly equal with  $[\text{Sn}^{2+}]_{tot}$  at the end of the titrations,  $[\text{Sn}^{2+}]_{tot} \approx 0.015 \text{ M}$  can be estimated. Using such a high  $[\text{Sn}^{2+}]_{tot}$  concentration  $\text{pH} \leq 2$  have to be used to prevent the hydrolysis of tin(II), but below  $\text{pH} \approx 3$  the protonation of fluoride ion should be taken into account, and this is not the case in [1968HAL/SLA]. Nevertheless, the experimental data given in [1968HAL/SLA] were re-evaluated for the purposes of this review. The following formation constants were obtained:  $\log_{10} \beta_1 = (4.60 \pm 0.24) (3\sigma)$ ,  $\log_{10} \beta_2 = (8.01 \pm 0.24)$ ,  $\log_{10} \beta_3 = (10.38 \pm 0.18)$  at  $t = 25 \text{ }^\circ\text{C}$ ;  $\log_{10} \beta_1 = (4.62 \pm 0.15) (3\sigma)$ ,  $\log_{10} \beta_2 = (7.92 \pm 0.21)$ ,  $\log_{10} \beta_3 = (10.40 \pm 0.15)$  at  $t = 45 \text{ }^\circ\text{C}$  and  $\log_{10} \beta_1 = (4.72 \pm 0.12) (3\sigma)$ ,  $\log_{10} \beta_2 = (8.73 \pm 0.09)$ ,  $\log_{10} \beta_3 = (10.47 \pm 0.24)$  at  $t = 60 \text{ }^\circ\text{C}$ . Considering the missing experimental details, the reported/recalculated formation constants were not considered any further in this review.

### [1968HOW/MOS]

Single crystals of tin(II) hydroxide oxide have been obtained. The crystals of tin(II) hydroxide oxide possess tetragonal symmetry. The space group is determined uniquely as  $P_4/mnc$ . The unit cell dimensions ( $a = (7.93 \pm 0.01)$ ,  $c = (9.13 \pm 0.01) \text{ \AA}$ ) refined by comparison with published diffraction data [1961DON/MOS], and the density of the material are compatible only with the presence of four formula units of  $3\text{SnO} \cdot \text{H}_2\text{O}$  per unit cell.

Donaldson and Moser [1961DON/MOS] have shown that there is only one stable solid tin(II) hydroxide, a unique crystalline phase quite distinct from other tin(II) oxides, which can be described as hydrous oxide or better tin(II) hydroxide oxide. The formula of the finely divided material was determined analytically as  $5\text{SnO} \cdot 2\text{H}_2\text{O}$ . Table A-22 shows that analytical results may not be able to distinguish between these and the alternative formula  $\text{Sn}_3\text{O}(\text{OH})_2$  of Howie and Moser [1968HOW/MOS].

Table A-22: Composition of tin(II) hydroxide oxide [1968HOW/MOS].

Composition	Sn <sub>3</sub> O(OH) <sub>2</sub>	Sn <sub>5</sub> O(OH) <sub>4</sub> [1961DON/MOS]
w(SnO)	95.73%	94.92%
w(H <sub>2</sub> O)	4.27%	5.08%

**[1968HSE/REC]**

The authors prepared a new Ag<sub>2</sub>S based membrane electrode to determine the sulfide ion concentration in aqueous solutions. The authors characterised the electrode, and then used it to determine the equilibrium constants for reaction



in 0.1 M NaNO<sub>3</sub> solution.

The electrode showed excellent sensitivity, but due to the high uncertainty of the first protonation constant of sulfide ion, the calibration of the electrode is questionable. Using  $\log_{10} K_1 = 14.44$  for the first protonation constants of sulfide ion, the authors determined  $\log_{10} K_{s,0}^\circ = -50.83$  for the solubility product of Ag<sub>2</sub>S. In [1989GAM/BAR], the authors recalculated the earlier reported  $\log_{10} K_{s,0}^\circ$  values for Ag<sub>2</sub>S, and determined  $\log_{10} K_{s,0}^\circ = -54.7$ , using  $\log_{10} K_1 = 18.57$  and  $\log_{10} K_2 = 6.99$  for the protonation constants of sulfide ion. Considering this  $\log_{10} K_{s,0}^\circ$  value, it is possible to recalibrate the electrode used in [1968HSE/REC]. In this way, however, the experimental data reported in [1968HSE/REC] result in negative concentrations for the dissolved SnS<sub>3</sub><sup>2-</sup> below pH 9. Refinement of the first protonation constant of sulfide ion, to obtain a coherent equilibrium constant for Reaction (A.38) for all experimental points, resulted in  $\log_{10} K((\text{A.38}), 298.15 \text{ K}) = (9.1 \pm 0.1)$ ,  $\log_{10} K_1 = 18.19$ , and is an excellent fit to the experimental data. The first protonation constant of sulfide ion determined in this way agrees well with the currently accepted thermodynamic value ( $\log_{10} K_1^\circ = (19.0 \pm 2.0)$ ), while  $\log_{10} K((\text{A.38}), 298.15 \text{ K})$  is similar to that re-evaluated from the data reported in [1956BAB/LIS]. Due to the high uncertainty of the first protonation constant of sulfide ion, the reviewers assigned a considerably higher uncertainty to  $\log_{10} K((\text{A.38}), 298.15 \text{ K}) (\pm 2.0, \text{ see Table IX-1})$ . Therefore, these reviewers prefer not to select a thermodynamic equilibrium constant for Reaction (A.38) based on these reports (see also the comments on [1956BAB/LIS]), but the recalculated values can be used until more data will be published on this system.

**[1969CAR]**

Electrophoretic measurements were carried out to study, among others, the complex formation between tin(II) and chloride ion at 25 °C. The author determined the migration of tin(II) as a function of the HCl concentration. The results indicated the formation of three complexes (SnCl<sup>+</sup>, SnCl<sub>2</sub>(aq) and SnCl<sub>3</sub><sup>-</sup>) up to  $[\text{HCl}]_{\text{tot}} = 0.9 \text{ m}$ . From the curve of the mobility the following constants were derived:  $\log_{10} \beta_1 = 1.05$ ,

$\log_{10} \beta_2 = 1.71$ ,  $\log_{10} \beta_3 = 1.69$ . Apparently the author took no special precaution to prevent the oxidation of tin(II). In addition, the ionic strength varied from 0.01 to 0.9 M during the measurements. Therefore, the reported constants were not considered any further in this review.

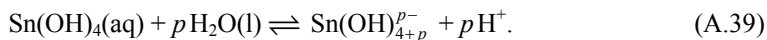
### [1969FED/BOL]

Potentiometric measurements using a tin amalgam electrode have been performed to study the formation of the tin(II)-bromido complexes at 25 °C in NaClO<sub>4</sub> media ( $I = 1.0, 2.0, 3.0, 4.0, 6.0$  and  $8.0$  M). Up to  $I = 4$  M, the formation of four bromido complexes ( $\text{SnBr}_q^{2-q}$ ,  $q = 1, 2, 3, 4$ ) was assumed to explain the experimental data, while the authors suggested the formation of six bromido species ( $q = 1$  to  $6$ ) at  $I = 8$  M. The Vasil'ev equation has been applied to extrapolate the  $\log_{10} \beta_q$  ( $q = 1$  to  $4$ ) values to  $I = 0$ . The background electrolyte (NaClO<sub>4</sub>) was entirely replaced by NaBr during the measurements, which resulted in a probably substantial change of the activity coefficients. Therefore, the reported experimental data were re-evaluated for the purposes of this review using the data points corresponding to at most 20% replacement of the background electrolyte ( $[\text{Br}^-]_{\text{tot}} \leq 0.2 I$ ). Considering the formation of  $\text{SnBr}^+$ ,  $\text{SnBr}_2(\text{aq})$  and  $\text{SnBr}_3^-$  the experimental data can be well reproduced up to  $I = 4$  M. At higher ionic strength a further species ( $\text{SnBr}_4^{2-}$ ) should be also taken into account. An uncertainty of  $\pm 0.3$  has been assigned to the recalculated  $\log_{10} \beta_q$  values.

### [1970BAR/KLI]

The solubility of cassiterite ( $\text{SnO}_2$ ) in pure water and in NaOH solutions was studied at 25 °C. Equilibrium between the solid and solution phases was established within a month. The dissolved tin(IV) was determined colorimetrically using *p*-nitrophenylfluorone, as well as by a polarographic method. Before the analysis, the volume of the aliquots was reduced by a factor 3 (by evaporation in presence of sulfuric acid), since the solubility of  $\text{SnO}_2$  in water is less than the detection limit of the method applied ( $0.5 \mu\text{g}\cdot\text{mL}^{-1}$  tin(IV)). The experimental data were explained by the formation of the complex  $\text{Sn}(\text{OH})_5^-$ .

The reported data were re-evaluated for the purposes of this review. The data are compatible with the formation of only  $\text{Sn}(\text{OH})_5^-$ :



The resulting constants are as follows:  $\log_{10} K_{s,0} = -(6.52 \pm 0.05)$  and  $\log_{10} \beta_{1,5}^*$  ((A.39),  $p = 1$ ) =  $-(11.28 \pm 0.09)$ , and  $\Delta a((\text{A.39}), p = 1, \text{NaOH}) = (0.03 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ . The solubility of  $\text{SnO}_2$  determined in pure water is considerably higher than that obtained in [1997AMA/CHI] and [1998ODA/AMA]. Probably the reason for this discrepancy is that despite of the sample treatment applied (volume reduction by evaporation) the concentration of tin(IV) in the samples was close to the detection limit. In alkaline solutions, the solubility of  $\text{SnO}_2$  was three log units smaller

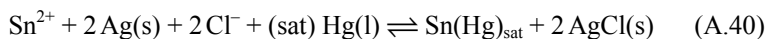


than in [1997AMA/CHI] and [1998ODA/AMA]. The reason of this difference is not clear. In [1970BAR/KLI] no information is given concerning the separation of the samples from CO<sub>2</sub> during the one-month equilibration. Since the hydroxide ion concentration was calculated from the initially added NaOH solutions, it is possible that the actual pH was significantly smaller than the calculated one, due to the dissolution of CO<sub>2</sub>. Therefore, the above listed re-evaluated constants were not used in the present review.

### [1970BON/TAY]

This paper reports d.c. and a.c. polarographic measurements on aqueous solutions containing Sn<sup>2+</sup> and F<sup>-</sup> ions. The results can be used to determine stability constants of fluoro complexes of tin(II). In addition the standard potential of Sn<sup>2+</sup>/Sn can be estimated from the polarographic half-wave potential of Sn<sup>2+</sup> + 2e<sup>-</sup> ⇌ Sn(0) vs. the reference electrode Ag/AgCl.

At 25 °C and I = 1.0 M NaClO<sub>4</sub> the authors found for Reaction (A.40)



$\Delta_r E^{\circ}$  (A.40) = -0.374 V. For reaction (A.41) [1967KRA] obtained in the same ionic medium



$\Delta_r E^{\circ}$  (A.41) = 0.23227 V. This leads to  $E_c^{\circ}$  (Sn<sup>2+</sup>/Sn(cr), 25 °C, I = 1.0 M NaClO<sub>4</sub>) = -(0.1407 ± 0.0020) V, when  $a_{\text{Sn}}$  in a saturated tin amalgam is accounted for [2003YEN/GRO]. The uncertainty of ± 0.0020 V has been estimated by the reviewers. With  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) = (0.19 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$ , Eq. (II.35) and Eq. (VI.5) lead to:

$$E_m^{\circ}(\text{Sn}^{2+}/\text{Sn}) = E_c^{\circ} + \left( \frac{RT \ln(10)}{nF} \right) \cdot \left[ \sum \nu_i \cdot \log_{10} \left( \frac{m_{\text{NaClO}_4}}{c_{\text{NaClO}_4}} \right) + 2D + \Delta\varepsilon \cdot m_{\text{ClO}_4^-} \right]$$

where  $\sum \nu_i = 1$ ,  $\Delta\varepsilon = 2\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-)$  and  $E^{\circ}(\text{Sn}^{2+}/\text{Sn}(\text{cr}), 298.15 \text{ K}) = -(0.1252 \pm 0.0027) \text{ V}$  has been obtained. Although this value is of the right order of magnitude it was not used for regression, because the results of [1917NOY/TOA], [1928PRY], [1938HAR/WHI], [1957WAK/SAL] and [1973VAS/GLA] appear to be better founded experimentally.

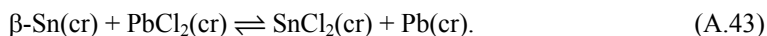
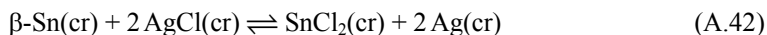
A remark with respect to the analysis of polarographic measurements seems to be in order. The uncertainty with respect to the equilibrium between Sn(Hg) ⇌ β-Sn + Hg(l) prevailing in this special case and the expected error of at least ± 1 mV render this method unsuitable for the determination of accurate and precise data.

Several polarographic (conventional and rapid a.c./d.c.) methods have been used to study the complex formation between tin(II) and fluoride ion in 1 M NaClO<sub>4</sub>

medium at acidic and neutral pH under inert atmosphere. Three complex species ( $\text{SnF}^+$ ,  $\text{SnF}_2(\text{aq})$ ,  $\text{SnF}_3^-$ ) have been identified. The half-wave potentials corresponding to the  $\text{Sn}^{2+}/\text{Sn}$  reduction have been determined as a function of the fluoride ion concentration. The so called Leden method (a graphical procedure) has been used to determine the formation constants of the complexes, using  $\text{p}K = 2.57$  for the ionisation constant of HF. This constant is somewhat different from the one which can be calculated from the selected NEA TDB values ( $\log_{10} K^\circ = 3.18$ ,  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Na}^+, \text{F}^-) = (0.02 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\log_{10} K(1 \text{ M NaClO}_4) = 2.94$ ). Therefore, the reported experimental data were re-evaluated, and the following formation constants were obtained:  $\log_{10} \beta_1 = (4.55 \pm 0.15) (3\sigma)$ ,  $\log_{10} \beta_2 = (6.8 \pm 1.0)$ ,  $\log_{10} \beta_3 = (9.43 \pm 0.10)$ . Under the conditions used, the species  $\text{SnF}_2(\text{aq})$  is always a minor complex, therefore its formation constant is not well defined. Considering the reported error of the measured half-wave potentials ( $\pm 1.5 \text{ mV}$ ), the uncertainties of  $\log_{10} \beta_1$  and  $\log_{10} \beta_3$  have been estimated to  $\pm 0.3$ .

### [1970BUG/SHE]

Bugden and Shelton [1970BUG/SHE] used displacement cells of the type  $\text{M} | \text{MCl}_n : \text{PbCl}_2 : \text{AgCl} | \text{Ag}$  and obtained the standard free energy of formation for the reactions:



The analysis is based on the following equations

$$\Delta_r H_m^\circ(298.15 \text{ K}) = \Delta_r G_m^\circ(T) + T \Delta_r S_m^\circ(T) - \Delta_r [H_m^\circ(T) - H_m^\circ(298.15 \text{ K})] \quad (\text{A.44})$$

$$S_m^\circ(T) = S_m^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T (C_p / T) dT \quad (\text{A.45})$$

$$H_m^\circ(T) = H_m^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T C_p dT \quad (\text{A.46})$$

The Gibbs energy functions  $\Delta_r G_m^\circ(T)$  were taken from [1970BUG/SHE], the standard entropies  $S_m^\circ(\text{AgCl}, \text{cr}, 298.15 \text{ K})$  and  $S_m^\circ(\text{Ag}, \text{cr}, 298.15 \text{ K})$  were taken from the selected auxiliary data in Table IV-1.

The standard entropies  $S_m^\circ(\text{Sn}, \beta, 298.15 \text{ K})$  and  $S_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})$ <sup>1</sup> as well as the heat capacity function  $[C_{p,m}^\circ]_{298.15 \text{ K}}^{505 \text{ K}}(\text{Sn}, \beta, T)$  have been selected in this review (see Sections V.1.3 and VIII.1.2.1). The heat capacity functions of  $\text{Ag}(\text{cr})$ ,  $\text{AgCl}(\text{cr})$ ,  $\text{Pb}(\text{cr})$  and  $\text{PbCl}_2(\text{cr})$  were calculated using values listed in [1991KNA/KUB]. The heat capacity function  $[C_{p,m}^\circ]_{289 \text{ K}}^{490 \text{ K}}(\text{SnCl}_2, \text{cr}, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 64.53 + 0.04523(T/\text{K})$  was obtained by linear least square analysis of experimental data given in [1979PAU/STE] and [1991GAR/PRE].

<sup>1</sup> The re-evaluation resulted in a slightly modified value for  $S_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) = 133.935 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The values of the standard enthalpies of formation  $\Delta_f H_m^\circ$  (AgCl, cr, 298.15 K) and  $\Delta_f H_m^\circ$  (PbCl<sub>2</sub>, cr, 298.15 K) were taken from selected auxiliary data in Table IV-1 and [1991KNA/KUB], respectively.

According to Table A-23, the molar standard enthalpy of Reaction (A.42) is  $\Delta_r H_m^\circ$  (A.42) =  $-(81.39 \pm 0.47)$  kJ·mol<sup>-1</sup>.

$$\begin{aligned}\Delta_f H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) &= \Delta_r H_m^\circ (\text{A.42}) + 2\Delta_f H_m^\circ (\text{AgCl}, \text{cr}, 298.15 \text{ K}) \\ &= -81.39 - 2 \times 127.01 \text{ kJ}\cdot\text{mol}^{-1} \\ &= -(335.41 \pm 0.48) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

According to Table A-24 the molar standard enthalpy of Reaction (A.43) is  $\Delta_r H_m^\circ$  (A.43) =  $(24.11 \pm 0.65)$  kJ·mol<sup>-1</sup>.

$$\begin{aligned}\Delta_f H_m^\circ (\text{SnCl}_2, \text{cr}, 298.15 \text{ K}) &= \Delta_r H_m^\circ (\text{A.43}) + \Delta_f H_m^\circ (\text{PbCl}_2, \text{cr}, 298.15 \text{ K}) \\ &= 24.11 - 359.405 \text{ kJ}\cdot\text{mol}^{-1} \\ &= -335.30 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The third-law method applied to Reactions (A.42) and (A.43) results in similar values for  $\Delta_f H_m^\circ$  (SnCl<sub>2</sub>, cr, 298.15 K), whereas the second-law values differ by 3.28 kJ·mol<sup>-1</sup>. The value of  $\Delta_f H_m^\circ$  (SnCl<sub>2</sub>, cr, 298.15 K) calculated from Reaction (A.42) shows a trend to higher values with increasing temperature (see Figure A-27), and the value of  $\Delta_f H_m^\circ$  (SnCl<sub>2</sub>, cr, 298.15 K) calculated from Reaction (A.43) shows a trend to higher values with decreasing temperature (see Figure A-28). As  $\Delta_f H_m^\circ$  (AgCl, cr, 298.15 K) is approved as TDB auxiliary datum, the third-law analysis of Reaction (A.42) can be considered to result in a more reliable value than Reaction (A.43). But the apparent temperature dependence of  $\Delta_f H_m^\circ$  (SnCl<sub>2</sub>, cr, 298.15 K) casts a shadow on the experimental data of [1970BUG/SHE].

Table A-23: Third-law analysis of the data of reaction  $\beta\text{-Sn}(\text{cr}) + 2\text{AgCl}(\text{cr}) \rightleftharpoons \text{SnCl}_2(\text{cr}) + 2\text{Ag}(\text{cr})$ .

T/K	SnCl <sub>2</sub> (cr)		Ag(cr)		AgCl(cr)		β-Sn(cr)		$-R \ln K_p^\circ$	$\Delta_f H_{298.15 \text{ K}}^\circ$
	$S^\circ(T)$	$\frac{-(H_T^\circ - H_{\text{ref}}^\circ)}{T}$	$S^\circ(T)$	$\frac{-(H_T^\circ - H_{\text{ref}}^\circ)}{T}$	$S^\circ(T)$	$\frac{-(H_T^\circ - H_{\text{ref}}^\circ)}{T}$	$S^\circ(T)$	$\frac{-(H_T^\circ - H_{\text{ref}}^\circ)}{T}$		
										J·K <sup>-1</sup> ·mol <sup>-1</sup>
										kJ·mol <sup>-1</sup>
298.15	133.935	0.000	42.550	0.000	96.250	0.000	51.180	0.000	-249.303	-81.68
300.00	134.418	-0.480	42.716	-0.157	96.580	-0.327	51.350	-0.167	-247.588	-81.67
350.00	146.626	-11.731	46.782	-3.763	104.790	-7.891	55.600	-4.086	-208.102	-81.37
400.00	157.505	-20.453	50.044	-6.500	112.060	-13.713	59.400	-7.133	-178.488	-81.32
450.00	167.369	-27.487	53.094	-8.656	118.660	-18.420	62.860	-9.604	-155.455	-81.19
490.00	174.673	-32.247	55.319	-10.082	123.590	-21.639	65.440	-11.296	-140.413	-81.12

Table A-24: Third-law analysis of the data of reaction  $\beta\text{-Sn}(\text{cr}) + \text{PbCl}_2(\text{cr}) \rightleftharpoons \text{SnCl}_2(\text{cr}) + \text{Pb}(\text{cr})$ .

T/K	SnCl <sub>2</sub> (cr)		Pb(cr)		PbCl <sub>2</sub> (cr)		β-Sn(cr)		-R ln K <sub>p</sub> <sup>o</sup>	Δ <sub>r</sub> H <sub>298.15 K</sub> <sup>o</sup>
	S <sup>o</sup> (T)	$\frac{-(H_T^o - H_{\text{ref}}^o)}{T}$	S <sup>o</sup> (T)	$\frac{-(H_T^o - H_{\text{ref}}^o)}{T}$	S <sup>o</sup> (T)	$\frac{-(H_T^o - H_{\text{ref}}^o)}{T}$	S <sup>o</sup> (T)	$\frac{-(H_T^o - H_{\text{ref}}^o)}{T}$		
J·K <sup>-1</sup> ·mol <sup>-1</sup>										
298.15	133.935	0.000	64.785	0.000	135.980	0.000	51.180	0.000	70.465	24.46
300.00	134.418	-0.480	64.951	-0.165	136.457	-0.476	51.350	-0.167	69.933	24.45
350.00	146.626	-11.731	69.121	-4.006	148.468	-11.541	55.600	-4.086	57.676	24.24
400.00	157.505	-20.453	72.792	-6.942	159.065	-20.021	59.400	-7.133	48.484	24.03
450.00	167.369	-27.487	76.081	-9.273	168.585	-26.777	62.860	-9.604	41.334	23.83
490.00	174.673	-32.247	78.493	-10.828	175.579	-31.297	65.440	-11.296	36.665	23.68

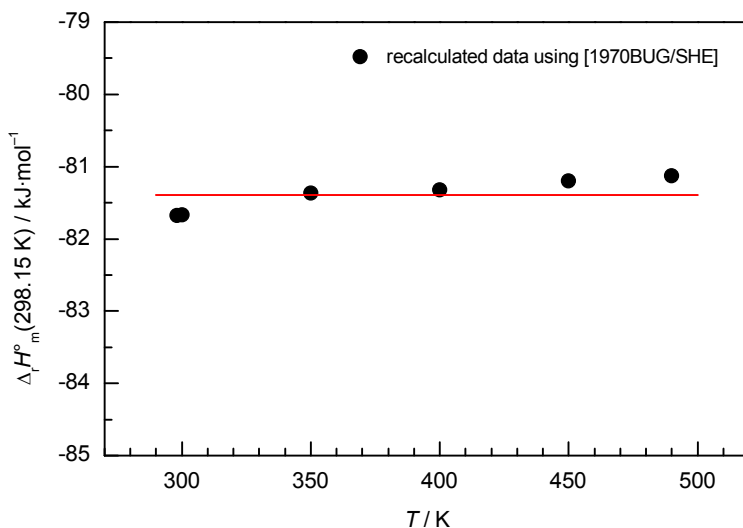
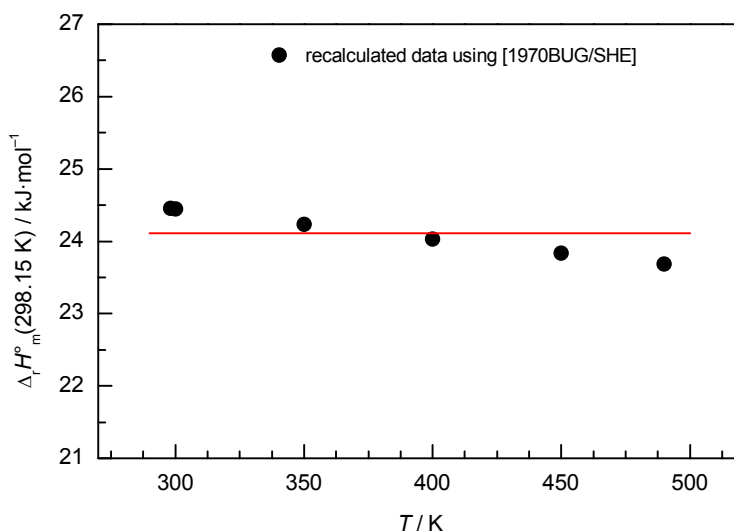
Figure A-27: Third-law analysis of the data of reaction  $\beta\text{-Sn}(\text{cr}) + 2\text{AgCl}(\text{cr}) \rightleftharpoons \text{SnCl}_2(\text{cr}) + 2\text{Ag}(\text{cr})$ .

Figure A-28: Third-law analysis of reaction  $\beta\text{-Sn}(\text{cr}) + \text{PbCl}_2(\text{cr}) \rightleftharpoons \text{SnCl}_2(\text{cr}) + \text{Pb}(\text{cr})$ .**[1970CHI]**

The formation of Mg(II)-, Ca(II)-, Zn(II)- and Cu(II)-phosphato complexes have been studied by potentiometric titrations at 37 °C. The formation of complexes with similar composition was suggested by the author, then reported for Sn(II) in [1968CIL] and [2000CIA/IUL2].

**[1970KUR/BAR]**

The solubility of Sn(IV) hydroxide in KOH and NaOH solutions depending on the pH at 100, 200 and 300 °C has been studied. The solubility decrease with rising temperature (up to  $2 \times 10^{-5}$  mol·dm<sup>-3</sup> Sn) is accompanied by a change of the composition of the solid phase which at 100 °C corresponds to varlamoffite, SnO<sub>2</sub>·xH<sub>2</sub>O and at 300 °C to cassiterite, SnO<sub>2</sub>. By the method of solubility the complexing in the systems Sn(OH)<sub>4</sub>-KOH-H<sub>2</sub>O and Sn(OH)<sub>4</sub>-NaOH-H<sub>2</sub>O at 100 °C has been investigated. In neutral and alkaline solutions (pH 7-11) complexes Sn(OH)<sub>4-i</sub><sup>i</sup> (where *i* is a positive or negative integer) are formed. Stability constants β<sub>*i*0</sub> of these complexes: β<sub>30</sub> = 5.0 × 10<sup>46</sup>, β<sub>40</sub> = 2.6 × 10<sup>51</sup>, β<sub>50</sub> = 4.0 × 10<sup>54</sup>, β<sub>60</sub> = 4.1 × 10<sup>57</sup>, have been calculated as well as their hydrolysis constants: K<sub>30</sub> = 2.9 × 10<sup>-8</sup>, K<sub>40</sub> = 8.7 × 10<sup>-10</sup>, K<sub>50</sub> = 5.7 × 10<sup>-10</sup>.

**[1970KUR/MAR]**

The solubility of freshly precipitated  $\text{Sn}(\text{OH})_4$  have been investigated by solubility method in NaF and KF solutions at different pH and at 300 °C and 90 atm.

Several experimental details are uncertain or doubtful: (i) the “freshly precipitated  $\text{Sn}(\text{OH})_4$ ” have not been characterised, (ii) the equilibration time was only 24 hours, (iii) the pH was measured by a glass electrode even in presence of HF, (iv) at a given  $[\text{F}^-]_{\text{tot}}$  concentration the solubility of  $\text{Sn}(\text{OH})_4(\text{s})$  showed several (2-3) extremes between pH 5.5 and 10, although monotonic change can be expected. The authors suggested the formation of polynuclear complexes through hydrogen-bond formation (F-HO), which is unlikely at concentration  $[\text{Sn}(\text{IV})]_{\text{tot}} = 6 - 20 \times 10^{-6} \text{ M}$ , (v) the authors detected fundamental differences between the measurements performed with NaF and KF, which is hard to explain.

**[1971NAZ/ANT]**

The hydrolysis constants of tin(IV) have been studied under acidic conditions (pH = 0.15 to 0.8) in 1 M  $\text{KNO}_3$  medium by a spectrophotometric method using salicylfluorone as competing ligand ( $[\text{Sn}(\text{IV})]_{\text{tot}} \sim 10^{-5} \text{ M}$ ). At  $I = 1.0 \text{ M}$  ( $\text{KNO}_3$ ) and  $T = (25 \pm 0.5) \text{ }^\circ\text{C}$  the following constants of hydrolysis had been determined:  $\beta_1 = 3.37 \times 10^{14}$ ,  $\beta_2 = 4.81 \times 10^{28}$ ,  $\beta_3 = 2.26 \times 10^{42}$ ,  $\beta_4 = 1.34 \times 10^{55}$ .

Results are tabulated for  $\text{Sn}(\text{IV}) = 8 \times 10^{-6} \text{ M}$ ,  $1.6 \times 10^{-5} \text{ M SF}$ .

The authors used simple glass electrodes to determine the pH, but the calibration method is not described in the paper. The use of glass electrodes at such a low pH is questionable. Due to the solubility of the salicylfluorone complex of tin(IV), the investigated solutions contained 8% ethanol and 0.04% gelatin. In addition, the possible interaction of tin(IV) with nitrate ion was neglected. Consequently, the data reported in this paper can be considered only as estimates, and cannot be used to derive selected values.

**[1971ORG/MAN]**

Tin pannikins lost from the overturned canoe of a voyageur between 1801 and 1821 were recovered. The surfaces of the pannikins have a thin crust of alteration products consisting of white and black crystals.

The black crystals give X-ray powder patterns practically identical to those given for  $\text{Sn}(\text{O}(\text{cr}))$ , romarchite.

The white crystals have an X-ray powder pattern which matches that of tin(II) oxide hydrate,  $5\text{SnO} \cdot 2\text{H}_2\text{O}(\text{cr})$ , hydroromarchite.

The minerals and names have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

**[1971PET2]**

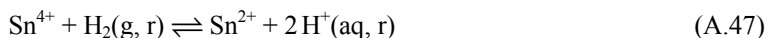
The interaction of molybdate with pyrophosphate ion have been studied by potentiometry. The author reported reliable dissociation constants of phosphoric acid in 3 M NaClO<sub>4</sub>.

**[1972DES/JOV]**

Equilibrium potentials of the redox couple Sn(IV)/Sn(II) on Hg were measured as functions of concentrations of Sn<sup>2+</sup>, Sn<sup>4+</sup>, Cl<sup>-</sup>, and H<sup>+</sup> in aqueous solutions containing 4 M HCl and 1 M Na<sub>2</sub>SO<sub>4</sub> + 1 M H<sub>2</sub>SO<sub>4</sub>, respectively. To identify the Sn(IV) species present in these solutions and to determine their stabilities, a method of analysis of potentiometric data was developed, based on the comparison of the Sn(IV) complexes with those of Sn(II) determined at  $I = 0$  by [1949RIC/POP]. The derived stability constants have been tabulated, and the calculated distribution of the Sn(IV) complexes as a function of the Cl<sup>-</sup> concentration has been presented.

In order to re-evaluate the results of [1972DES/JOV] Figures 2, 3 and 5 of this paper have been digitalised.

From Figure 2 equilibrium potentials of Reaction (A.47)



in solutions (I) and (II) were obtained. In Eq. (A.47) "r" is used to indicate that H<sub>2</sub>(g) and H<sup>+</sup>(aq) are at the chemical conditions in the reference electrode compartment, see Eq. (B.14).

I: [Sn(IV)] = 1.0 × 10<sup>-1</sup> M, [HCl] = 4.0 M, [Sn(II)] = 0.003 to 1.0 M.

II: [Sn(IV)] = 1.0 M, [HCl] = 4.0 M, [Sn(II)] = 0.0003 to 1.0 M.

Figure 3 provides equilibrium potentials of Reaction (A.47) in solutions (III) and (IV).

III: [Sn(II)] = 1.0 × 10<sup>-1</sup> M, [HCl] = 4.0 M, [Sn(IV)] = 0.001 to 1.0 M.

IV: [Sn(II)] = 1.0 M, [HCl] = 4.0 M, [Sn(IV)] = 0.001 to 1.0 M.

Figure 5 contains equilibrium potentials of Reaction (A.47) in solutions (V). V: [Na<sub>2</sub>SO<sub>4</sub>] = 1.0 M, [H<sub>2</sub>SO<sub>4</sub>] = 1.0 M, [Sn(IV)] = [Sn(II)] = 0.01 M, [Cl<sup>-</sup>] = 0.06 to 3.0 M.

The equilibrium potentials of Reaction (A.47) in solutions (V) can be represented by Eq. (A.48).

$$E = E_{\text{V}}^{\circ} (\text{Sn}^{4+}/\text{Sn}^{2+}) - (RT/2F) \cdot \ln(10) \cdot \log_{10} \{ [\text{Sn}^{2+}]/[\text{Sn}^{4+}] \} \quad (\text{A.48})$$

According to Despić *et al.* the total concentrations of di- and tetravalent tin can be expressed by

$$[\text{Sn(II)}] = [\text{Sn}^{2+}] + [\text{SnCl}^+] + [\text{SnCl}_2] + [\text{SnCl}_3^-] + [\text{SnCl}_4^{2-}]$$

$$[\text{Sn(II)}] = [\text{Sn}^{2+}] \cdot \{1 + [\text{Cl}^-] \cdot (\beta_{1(2)} + \beta_{2(2)} \cdot [\text{Cl}^-] + \beta_{3(2)} \cdot [\text{Cl}^-]^2 + \beta_{4(2)} \cdot [\text{Cl}^-]^3)\}$$

$$[\text{Sn(IV)}] = [\text{Sn}^{4+}] + [\text{SnCl}^{3+}] + [\text{SnCl}_2^{2+}] + [\text{SnCl}_3^+] + [\text{SnCl}_4] + [\text{SnCl}_5^-]$$

$$[\text{Sn(IV)}] = [\text{Sn}^{4+}] \cdot \{1 + [\text{Cl}^-] \cdot (\beta_{1(4)} + \beta_{2(4)} \cdot [\text{Cl}^-] + \beta_{3(4)} \cdot [\text{Cl}^-]^2 + \beta_{4(4)} \cdot [\text{Cl}^-]^3 + \beta_{5(4)} \cdot [\text{Cl}^-]^4)\}.$$

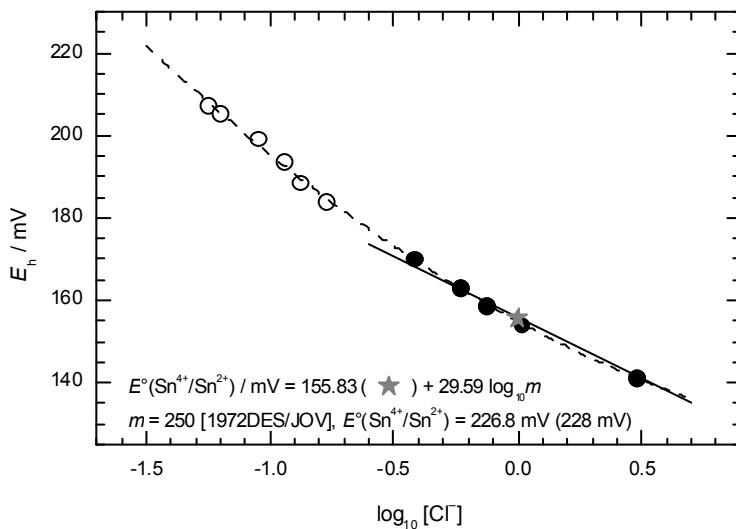
In the range  $[\text{Cl}^-] \geq 0.32 \text{ M}$   $\text{SnCl}_2$ ,  $\text{SnCl}_3^-$ ,  $\text{SnCl}_4^{2-}$  and  $\text{SnCl}_5^-$ ,  $\text{SnCl}_4$ ,  $\text{SnCl}_5^-$ , respectively are the dominant species. Moreover  $\beta_{3(4)}/\beta_{2(2)} = \beta_{4(4)}/\beta_{3(2)} = \beta_{5(4)}/\beta_{4(2)} = \text{const}$ . In this case Eq. (A.48) transforms into

$$E_h = E_v^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}) - (k/2) \cdot \{\log_{10} ([\text{Sn(II)}]/[\text{Sn(IV)}]) + \log_{10} [\text{Cl}^-] + \log_{10} m\} \quad (\text{A.49})$$

where  $(RT/2F) \ln(10)$  has been abbreviated to  $(k/2)$ .

A plot of  $E_h$  vs.  $\log_{10} [\text{Cl}^-]$  at  $\log_{10} ([\text{Sn(II)}]/[\text{Sn(IV)}]) = 0$  becomes indeed linear for  $\log_{10} [\text{Cl}^-] \geq 0.38$  and coincides reasonably with the theoretical slope =  $-29.59 \text{ mV}$ , see Figure A-29.

Figure A-29: Variation of  $E_h$  as a function of  $\log_{10} [\text{Cl}^-]$ . Experimental data of [1972DES/JOV] at  $25^\circ \text{C}$  ( $\circ$ ,  $\bullet$ :  $[\text{Sn}^{2+}] = [\text{Sn}^{4+}] = 0.01 \text{ M}$ , solid line: linear regression).



When the value ( $m = 250$ ,  $\log_{10} m = 2.4$ ) given by Despić *et al.* is used  $E_v^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}) = 226.8 \text{ mV}$  agrees nicely with  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}) = 228 \text{ mV}$  according to [1972DES/JOV]. In this paper it has not been unambiguously demonstrated, however, that  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+})$  and  $m$  have been determined independently of one another. The index V of  $E^\circ$  indicates that neither the inert electrolyte nor the ionic strength of



solutions (V) and solutions (I) to (IV) agree with each other. To check whether the assumption

$$\log_{10} ([\text{Sn}^{2+}]/[\text{Sn}^{4+}]) = \log_{10} ([\text{Sn(II)}]/[\text{Sn(IV)}]) + \log_{10} [\text{Cl}^-] + (2.4 \pm 0.2) \quad (\text{A.50})$$

is valid in the 4 M HCl containing solutions (I) to (IV) as well, the equilibrium potentials measured in these solutions were re-evaluated separately, see Figure A-30 and Figure A-31.

The mean value of  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+})$  has been calculated assuming that Eq. (A.50) is correct and 4 M HCl is the constant ionic medium in solutions (I) to (IV).

The re-evaluation of the digitalised data resulted in  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+}, 4 \text{ M HCl}, 298.15 \text{ K}) = (225.3 \pm 6.1) \text{ mV}$ , the calculated uncertainty, see Table A-25, seems to be realistic in view of Eq. (A.50). It is unlikely that the uncertainty of  $\log_{10} m$  is less than  $\pm 0.2$ , consequently the uncertainty of  $E^\circ$  was expected to be  $\pm 6 \text{ mV}$ . The assumption of this paper is certainly questionable that reliable stability constants of Sn(IV) chlorido complexes in 4 M HCl and 1 M  $\text{Na}_2\text{SO}_4 + 1 \text{ M H}_2\text{SO}_4$ , respectively can be based on stability constants of Sn(II) chlorido complexes valid at  $I = 0$  [1949RIC/POP]. As the calculations are internally consistent, Eq. (A.50) might be applicable for the evaluation of  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+})$  from other cell-potential data in HCl media, e.g. [1914FOR/BAR] and [1934HUE/TAR], if  $m$ , see Eq. (A.49), can be determined independently.

Figure A-30: Variation of  $E_h$  as a function of  $\log_{10} [\text{Sn}^{2+}]$ . Experimental data of [1972DES/JOV] at 25 °C (○, ●:  $[\text{Sn(IV)}] = 0.1 \text{ M}$ ; □, ■:  $[\text{Sn(IV)}] = 0.01 \text{ M}$ ; solid lines: linear regression analyses). Only solid symbols have been considered for regression analysis.

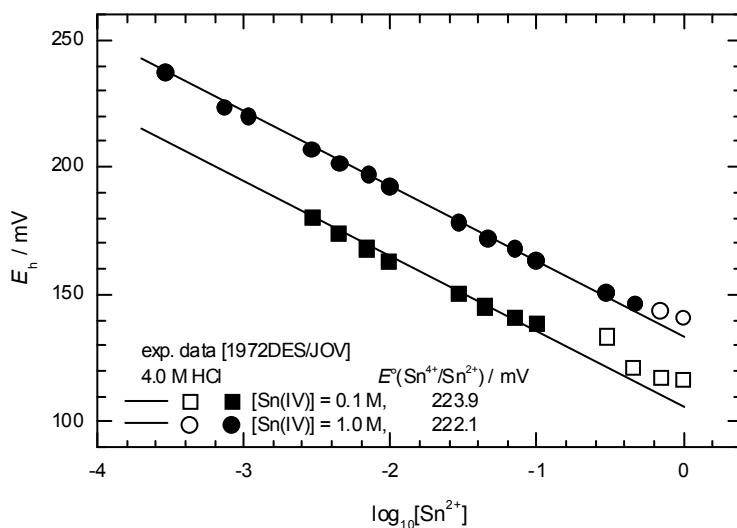


Figure A-31: Variation of  $E_h$  as a function of  $\log_{10} [\text{Sn}^{4+}]$ . Experimental data of [1972DES/JOV] at 25 °C (○, ●:  $[\text{Sn(II)}] = 0.1 \text{ M}$ ; □, ■:  $[\text{Sn(II)}] = 0.01 \text{ M}$ ; solid lines: linear regression analyses). Only solid symbols have been considered for regression analysis.

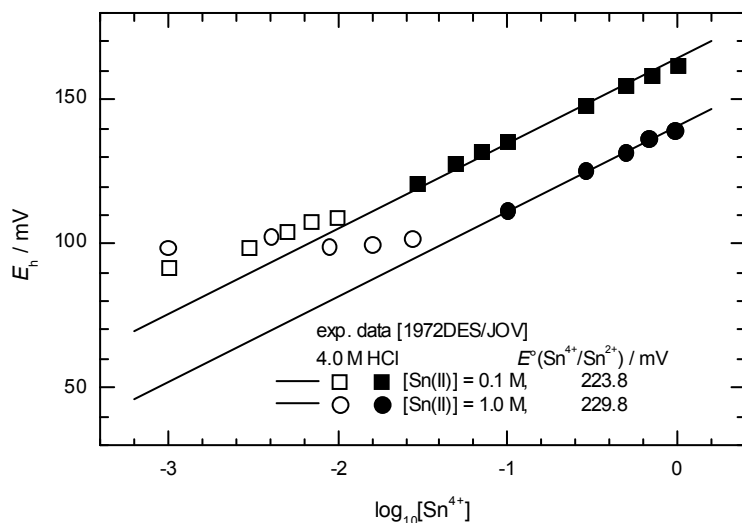


Table A-25: Consistency test for  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+})$  measurements.

	No.	$E^\circ / \text{mV}$	$\sigma$	$(E^\circ - \bar{E}^\circ)^2 / \text{mV}^2$
solution (I)	1	223.92	$\pm 1.36$	1.8496
solution (II)	2	223.81	$\pm 1.47$	2.1609
solution (III)	3	229.78	$\pm 4.50$	20.2500
solution (IV)	4	222.09	$\pm 3.19$	10.1761
solution (V)	5	226.80	$\pm 1.52$	2.3104
		$\bar{E}^\circ$	$2\sigma$	$\sum (E^\circ - \bar{E}^\circ)^2$
		<b>225.28</b>	<b><math>\pm 6.06</math></b>	36.7470

For comparison with other potentiometric measurements on Reaction (A.47), the data were converted to the molality scale.

$$E_m^\circ = E - (RT/2F) \cdot \ln(10) \cdot \log_{10}(m_{\text{Sn(II)}}/m_{\text{Sn(IV)}})$$

for the sake of brevity  $(RT/2F) \cdot \ln(10)$  has been replaced by  $k/2$ . In Table A-26  $E^\circ$  corrections by the [1972DES/JOV] approach or the Debye-Hückel term are

compared. It is interesting to note that the values do not differ greatly although the former refer to molality products and the latter to activity.

Table A-26: Comparison of  $E^\circ$  corrections.

$I/m$	$m_{\text{Cl}^-}$	$E_{\text{app}, I}^\circ / \text{mV}$	$(E_{\text{app}, I}^\circ + (k/2) \cdot \{\log_{10} m_{\text{Cl}^-} + m\}) / \text{mV}$	$(E_{\text{app}, I}^\circ + (k/2) \cdot 12D) / \text{mV}$
5.615	4.918	134.94	226.44	228.99
6.257	5.251	136.99	229.33	232.14
14.644	9.706	135.65	235.89	238.28
17.163	9.835	132.67	233.08	236.48

The ionic strength changed during these measurements,  $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$  cannot be regarded as inert electrolyte, and the stability constants of the chlorido complexes were evaluated in a doubtful way. Consequently the results were finally rejected.

#### [1973DAN/CHI]

The hydrolytic precipitation of iron(III) has been investigated at 25 °C in a 1 M (Na)NO<sub>3</sub> medium by measuring the acidity of solutions by glass electrode potentiometry. The data could be explained by assuming only the reaction  $\text{Fe}^{3+} + \text{NO}_3^- + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe}(\text{OH})_2\text{NO}_3(\text{s}) + 2\text{H}^+$  with  $\log_{10} {}^*K_s = -(2.20 \pm 0.03)$ .

This paper is cited by [1995DJU/JEL] and these authors used the same method of thermodynamic analysis to assign stoichiometry and stability constant to the hydrolytic precipitate of tin(II) in a 3 M (Na)Cl medium.

#### [1973HOW/MOS]

In this short note it is pointed out that the crystal data on tin(II) hydroxide oxide of [1961DON/MOS] have been superseded by data from single crystal measurements on better crystals [1968HOW/MOS]. The primitive tetragonal unit cell dimensions are  $a = 7.98(1) \text{ \AA}$  and  $c = 9.17(1) \text{ \AA}$ , and the space group is  $P4/mnc$  or  $P4/nc$ . The structural units ( $\text{Sn}_6\text{O}_8$  – two per unit-cell) are hydrogen bonded to one another (O–O between units 2.80 Å) so that the structural units are  $\text{Sn}_6(\text{OH})_4\text{O}_4$ , corresponding to an analytical formula  $3\text{SnO} \cdot \text{H}_2\text{O}$ .

#### [1973HUL/DES]

A comprehensive and detailed review and critical evaluation of the experimental data on thermodynamic properties of tin to 1970. Properties include: phases, structure, heat capacity of solid, liquid and gas as functions of temperature, superconducting transition temperature, electronic contribution coefficient, enthalpies and temperatures of transition, enthalpies of solid, liquid and gas, standard and temperature dependent

entropies, Gibbs energy function and vapour pressure. Recommended data are tabulated in the temperature range 0 to 3000 K.

### [1973KLI/BAR]

The solubility of synthetic cassiterite ( $\text{SnO}_2$ ) in pure water at 25, 100, 200 and 300 °C, and in 0.05 to 0.5 M NaOH solutions at 200 °C was studied using an autoclave. The equilibrium between the solid and solution phases was established within 20 days at 100 °C, and within ten days at 200 °C. The dissolved tin(IV) was determined colorimetrically using phenylfluoron and p-nitrophenylfluorone. The detection limit, reported by the authors, is 0.08  $\mu\text{g}\cdot\text{ml}^{-1}$  tin(IV) (in [1970BAR/KLI] 0.5  $\mu\text{g}\cdot\text{ml}^{-1}$  is given for the same method). The experimental data indicated only formation of the complex  $\text{Sn}(\text{OH})_6^{2-}$ . The solubility of  $\text{SnO}_2$  both in water and in alkaline solutions (as compared to the data reported in [1970BAR/KLI]) increased with increasing temperature. From the measured solubility at different temperatures  $\Delta_r H_m^\circ = 14.3 \text{ kJ}\cdot\text{mol}^{-1}$  was determined for the enthalpy of reaction  $\text{SnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_4$ .

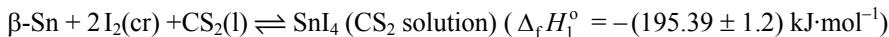
Using the  $\log_{10} {}^*\beta_{q,1}$  ( $q = 1$  to 4) values reported in [1971NAZ/ANT] for  $I = 1.0 \text{ M NaNO}_3$  and the Vasil'yev coefficient (b) determined for the hydrolysis of Ge(IV), the authors calculated the thermodynamic hydrolysis constants of tin(IV), by means of the SIT related Vasil'yev equation:  $\log_{10} {}^*\beta_{1,1}^\circ = 0.49$ ,  $\log_{10} {}^*\beta_{2,1}^\circ = 0.30$ ,  $\log_{10} {}^*\beta_{3,1}^\circ = -0.58$ ,  $\log_{10} {}^*\beta_{4,1}^\circ = -2.61$ .

Since even the original data of [1971NAZ/ANT] are only estimates, the above  $\log_{10} {}^*\beta_{q,1}$  values cannot be accepted.

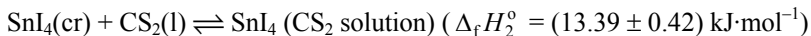
The solubility data determined in NaOH solution at 200 °C have been re-evaluated for the purposes of this review, using  $\text{p}K_w = 11.2$  for  $I = 0$  and  $T = 200 \text{ }^\circ\text{C}$ . The non-linear curve fitting of the data points resulted in the following constants:  $\log_{10} K_{s,0} = -(5.52 \pm 0.06)$ ,  $\log_{10} {}^*\beta_{6,1}^\circ (\text{Sn}(\text{OH})_4 + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_6^{2-} + 2 \text{H}^+) = -(20.16 \pm 0.09)$ , and  $\Delta a (\text{Sn}(\text{OH})_4 + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_6^{2-} + 2 \text{H}^+, \text{NaOH}) = -(0.81 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$  (see Figure A-32). Since the determined solubility of  $\text{SnO}_2$  in alkaline solutions at 200 °C is lower than can be expected from the values selected in this review at 25 °C, the above constants can be regarded only as estimates.

### [1973MIK]

Mikler [1973MIK] measured the enthalpy change at 298.15 K for the reactions involving iodine and  $\text{CS}_2$ . They first measured the enthalpy of formation of  $\text{SnI}_4$  from elements in solution according to the reaction:

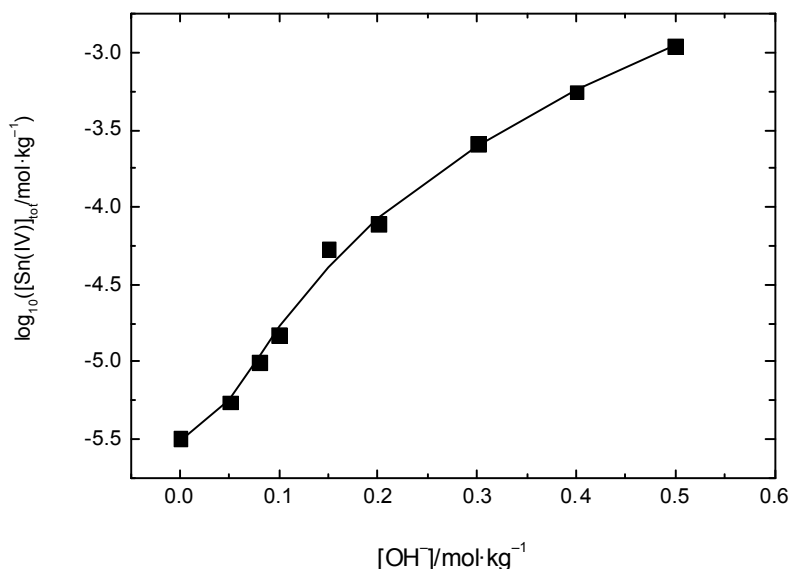


and then



to arrive at  $\Delta_f H_m^\circ(\text{SnI}_4, \text{cr}, 298.15 \text{ K}) = -(208.78 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ . Their calculated entropy of  $291.63 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is not based on the latest heat capacity data [1974ANI/STE] and is therefore significantly different from the one adopted in this review. They adopted the data for  $\text{SnI}_2(\text{cr})$  from [1968WAG/EVA].

Figure A-32: Solubility of  $\text{SnO}_2$  in  $\text{NaOH}$  solutions.



#### [1973MUR/TRO]

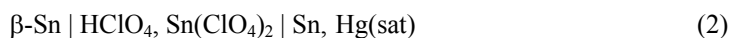
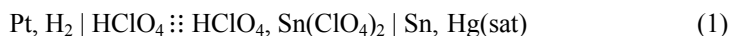
The thermal decomposition of  $\text{SnO}$  by heating within 1 h to  $450^\circ\text{C}$  and keeping 90 min at  $450^\circ\text{C}$  gave  $\text{Sn}_2\text{O}_3$  an instable intermediate phase which disproportionated to  $\text{Sn}$  and  $\text{SnO}_2$  on further heating.  $\text{Sn}_2\text{O}_3$  had lattice constants  $a = 5.457$ ,  $b = 8.179$ , and  $c = 3.714 \text{ \AA}$ ,  $\rho(\text{exptl.}) = 5.90 \text{ g}\cdot\text{cm}^{-3}$ , and  $\rho(\text{calcd.}) = 5.73 \text{ g}\cdot\text{cm}^{-3}$ .

#### [1973VAS/GLA]

The standard potential for the following reaction



was determined in aqueous perchloric acid solutions using cells (1) and (2)



The potential difference of these cells were measured at 15, 25 and 35 °C in a concentration range of 1.0, 2.0, 3.0, 4.0 M HClO<sub>4</sub> and 0.017 to 0.11 M Sn(ClO<sub>4</sub>)<sub>2</sub>. The standard potentials found at 15 (–141.5 mV), 25 (–144.5 mV) and 35 °C (–146.8 mV) were used to calculate  $\Delta_r G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.87 \pm 0.08) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r S_m^\circ(\text{A.51}) = -(51.1 \pm 9.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and  $S_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(27.6 \pm 9.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

While the value of  $\Delta_r G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  is close to the one selected by CODATA [1989COX/WAG] (–(27.60 ± 0.40) kJ·mol<sup>–1</sup>) the value of  $S_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  has been obtained by deriving  $\partial E^\circ/\partial T$  from only three data pairs. It deviates considerably from the CODATA value (–(16.7 ± 4.0) J·K<sup>–1</sup>·mol<sup>–1</sup>) and cannot be recommended for selection.

Vasil’ev and Glavina’s experimental data have been re-evaluated with the SIT model. The densities of HClO<sub>4</sub> solutions at  $t = 15$  and 35 °C were interpolated from the data given at 10, 20 and 30, 40 °C in [1989LOB], respectively. This SIT analysis, see Figure A-33, Figure A-34, Figure A-35, resulted in a value for  $\Delta_r G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -(28.01 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$ , slightly different to the one given by Vasil’ev and Glavina. In addition the values of  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-)$  were calculated for 15, 25 and 35 °C (see Table A-27).

Figure A-33: SIT analysis of the data of [1973VAS/GLA] at 15 °C (▼: experimental data, error bars (±0.5 mV) estimated by the reviewer; solid line: linear fit; dotted lines: 95% confidence limits).

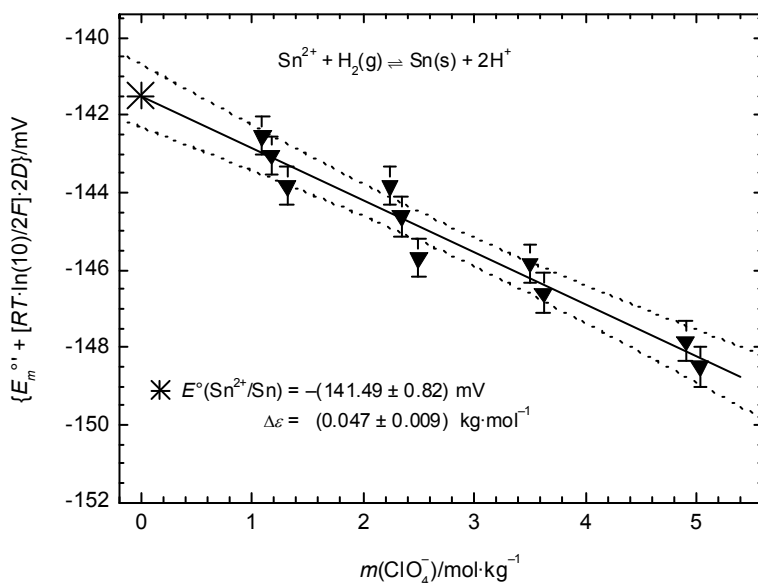


Figure A-34: SIT analysis of the data of [1973VAS/GLA] at 25 °C (●: experimental data, error bars ( $\pm 0.5$  mV) estimated by the reviewer; solid line: linear fit; dotted lines: 95% confidence limits).

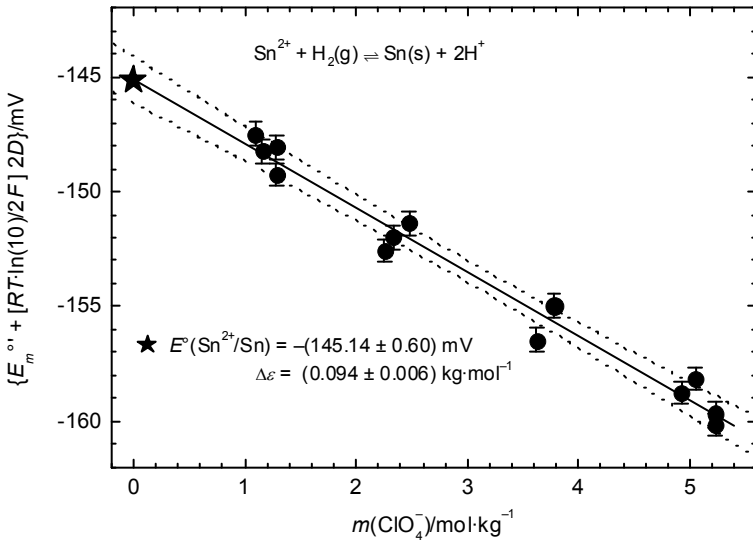


Figure A-35: SIT analysis of the data of [1973VAS/GLA] at 35 °C (●: experimental data, error bars ( $\pm 0.5$  mV) estimated by the reviewer; solid line: linear fit; dotted lines: 95% confidence limits).

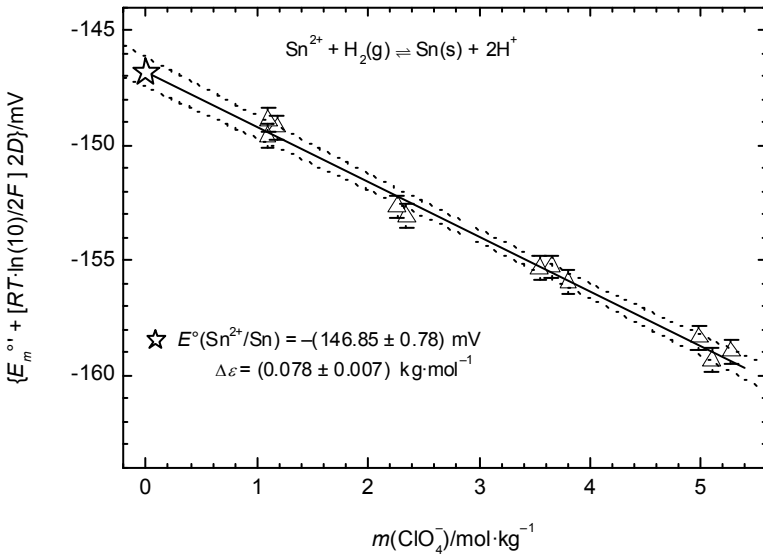
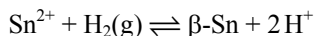


Table A-27: Value of  $\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-)$  for variable temperature.

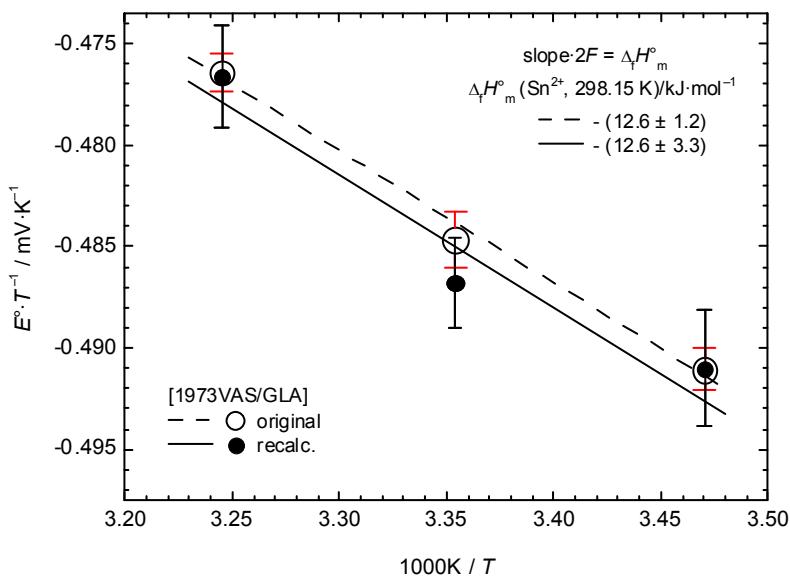
$t/^\circ\text{C}$	$\Delta\varepsilon = 2\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) / \text{kg}\cdot\text{mol}^{-1}$	$\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) / \text{kg}\cdot\text{mol}^{-1}$
15	$0.047 \pm 0.009$	$0.23 \pm 0.04$
25	$0.094 \pm 0.006$	$0.19 \pm 0.04$
35	$0.078 \pm 0.007$	$0.20 \pm 0.04$

The reported and recalculated values of the standard electrode potential  $E^\circ$  for



were used to estimate  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$ , see Figure A-36. For the determination of a reliable value of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  more data pairs  $E^\circ, T$  over a wider temperature range would be needed.

Figure A-36: Determination of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$ . (○: original experimental data of [1973VAS/GLA], error bars as given by the authors; dashed line: linear fit of the experimental data weighted by uncertainties; ●: experimental data recalculated by this review, error bars estimated by the reviewer; solid line: linear fit of the recalculated data weighted by uncertainties).

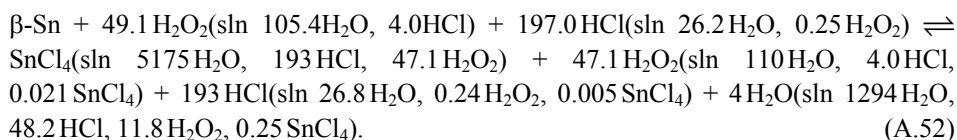




**[1973VAS/KOK]**

The heats of dissolution of metallic tin in hydrochloric acid solutions of hydrogen peroxide have been measured calorimetrically at 25 °C and ionic strengths 1, 2, 3, and 4 M HCl. The enthalpies of formation of SnCl<sub>4</sub> in these solutions have been calculated.

According to the authors a typical dissolution experiment can be represented by the following equation:



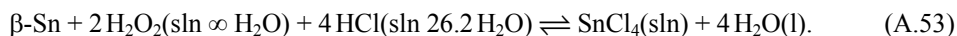
The slight stoichiometric inconsistencies in Eq. (A.52) above are inconsequential and due to rounding errors.

$$\Delta_f H_m^\circ (\text{H}_2\text{O}_2, \text{sln } 105.4\text{H}_2\text{O}, 4.0 \text{HCl}) = \Delta_f H_m^\circ (\text{H}_2\text{O}_2, \text{sln } 110\text{H}_2\text{O}, 4.0\text{HCl}, 0.021 \text{SnCl}_4) = \Delta_f H_m^\circ (\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O}),$$

$$\Delta_f H_m^\circ (\text{HCl}, \text{sln } 26.2\text{H}_2\text{O}, 0.25 \text{H}_2\text{O}_2) = \Delta_f H_m^\circ (\text{HCl}, \text{sln } 26.8\text{H}_2\text{O}, 0.24 \text{H}_2\text{O}_2, 0.005 \text{SnCl}_4) = \Delta_f H_m^\circ (\text{HCl}, \text{sln } 26.2 \text{H}_2\text{O})$$

$$\Delta_f H_m^\circ (\text{H}_2\text{O}, 0.037 \text{HCl}, 0.009 \text{H}_2\text{O}_2, 0.0002 \text{SnCl}_4) = \Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l}).$$

Consequently Eq. (A.52) can be simplified to Eq. (A.53)



Thus the enthalpy of formation of SnCl<sub>4</sub> in these solutions can essentially be obtained by Eq. (A.54):

$$\Delta_f H_m^\circ (\text{SnCl}_4, \text{sln}) = \Delta_f H_m^\circ (\text{A.52}) - 4\Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l}) + 2\Delta_f H_m^\circ (\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O}) + 4\Delta_f H_m^\circ (\text{HCl}, \text{sln } 26.2 \text{H}_2\text{O}). \quad (\text{A.54})$$

Using the value for  $\Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l})$  given by CODATA [1989COX/WAG] and the values for  $\Delta_f H_m^\circ (\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O})$  and  $\Delta_f H_m^\circ (\text{HCl}, \text{sln } 26.2\text{H}_2\text{O})$  given by [1982WAG/EVA] essentially the same results were obtained as those listed by the authors (Table A-28).

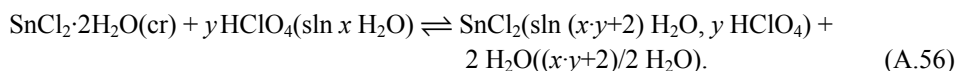
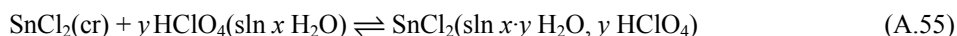
The results of this work are the basis for the determination of standard enthalpies of formation of tin compounds, and are accepted by the Review Team for recalculations.

Table A-28: Standard enthalpies of formation of SnCl<sub>4</sub> in HCl, H<sub>2</sub>O<sub>2</sub> solutions ( $r = n_i/n(\text{SnCl}_4)$ ).

[HCl]/M	$r(\text{H}_2\text{O}_2)$	$r(\text{HCl})$	$r(\text{H}_2\text{O})$	$-\Delta_f H_m^\circ(\text{SnCl}_4, \text{sln}, 295.15 \text{ K})/\text{kcal}\cdot\text{mol}^{-1}$
1.0	50	100	5400 – 5700	152.1 ± 0.6
2.0	50	200	5000 – 5500	151.2 ± 0.8
3.0	50	300	5200 – 5400	149.9 ± 0.7
4.0	50	400	5000 – 5300	149.9 ± 1.0
1.0	85	100	5100 – 5200	152.2 ± 0.4
2.0	85	200	5000 – 5300	152.1 ± 0.5
3.0	85	300	4900 – 5200	149.9 ± 0.7
4.0	85	400	4800 – 5300	149.9 ± 1.5

**[1973VAS/VAS]**

The standard enthalpy of formation of tin(II) chloride in perchloric acid solutions has been investigated calorimetrically. The following reactions were investigated:



The standard enthalpy of tin(II) chloride in perchloric acid solutions has been calculated by

$$\Delta_f H_m^\circ(\text{SnCl}_2, \text{sln}, 298.15 \text{ K}) = \Delta H_1 + \Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})$$

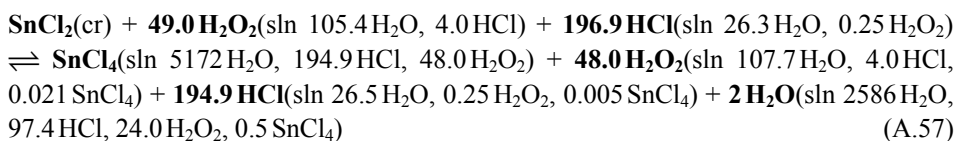
$$\Delta_f H_m^\circ(\text{SnCl}_2, \text{sln}, 298.15 \text{ K}) = \Delta H_2 + \Delta_f H_m^\circ(\text{SnCl}_2\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) - 2\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}).$$

$\Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ(\text{SnCl}_2\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  were taken from [1973VAS/VAS2]. The values obtained for  $\Delta_f H_m^\circ(\text{SnCl}_2, \text{sln}, 298.15 \text{ K})$  agreed within the experimental error with each other regardless whether SnCl<sub>2</sub>(cr) or SnCl<sub>2</sub>·2H<sub>2</sub>O(cr) were used as starting materials. No final result of this work was explicitly given, but the information obtained was used for thermochemical studies on Sn<sup>2+</sup> and SnCl<sup>+</sup> ions [1976VAS/KOK]. The present paper, however, is most valuable, because it contains experimental details regarding the composition of the solutions employed, the prerequisite for recalculation of  $\Delta_f H_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ(\text{SnCl}^+, 298.15 \text{ K})$ .

**[1973VAS/VAS2]**

The heats of dissolution of SnCl<sub>2</sub>(cr) and SnCl<sub>2</sub>·2H<sub>2</sub>O(cr) in HCl solutions containing H<sub>2</sub>O<sub>2</sub> have been measured at 25 °C and the standard enthalpies of formation of these salts have been calculated using the results of [1973VAS/KOK].

According to the authors a typical dissolution experiment can be represented by the following equation:



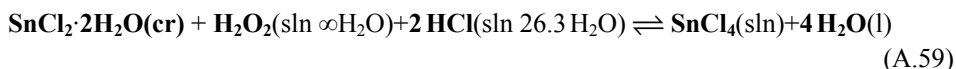
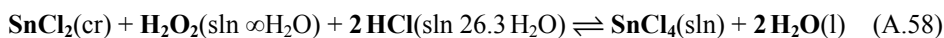
For stoichiometric inconsistencies in Eq. (A.57), see Appendix A entry for [1973VAS/KOK].

$$\begin{aligned} \Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } 105.4 \text{H}_2\text{O}, 4.0 \text{HCl}) &= \Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } 107.7 \text{H}_2\text{O}, 4.0 \text{HCl}, \\ &\quad 0.021 \text{SnCl}_4) \\ &= \Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O}) \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.3 \text{H}_2\text{O}, 0.25 \text{H}_2\text{O}_2) &= \Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.5 \text{H}_2\text{O}, 0.25 \text{H}_2\text{O}_2, \\ &\quad 0.005 \text{SnCl}_4) \\ &= \Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.3 \text{H}_2\text{O}) \end{aligned}$$

$$\Delta_f H_m^\circ(\text{H}_2\text{O}, 0.038 \text{HCl}, 0.009 \text{H}_2\text{O}_2, 0.0002 \text{SnCl}_4) = \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$$

Consequently Eq. (A.57) and the analogous equation for  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  can be simplified to Eqs. (A.58) and (A.59).



The respective enthalpies of formation were obtained by

$$\begin{aligned} \Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}) &= \Delta_f H_m^\circ(\text{SnCl}_4, \text{sln}) + 2\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) \\ &\quad - 2\Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.3 \text{H}_2\text{O}) - \Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O}) \\ &\quad - \Delta_{\text{diss}} H^\circ \quad (\text{A.58}) \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}) &= \Delta_f H_m^\circ(\text{SnCl}_4, \text{sln}) + 4\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) \\ &\quad - 2\Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.3 \text{H}_2\text{O}) - \Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O}) \\ &\quad - \Delta_{\text{diss}} H^\circ \quad (\text{A.59}). \end{aligned}$$

Using the value for  $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$  given by CODATA [1989COX/WAG] and the values for  $\Delta_f H_m^\circ(\text{H}_2\text{O}_2, \text{sln } \infty \text{H}_2\text{O})$  and  $\Delta_f H_m^\circ(\text{HCl}, \text{sln } 26.3 \text{H}_2\text{O})$  given by [1982WAG/EVA] essentially the same results were obtained as those listed by the authors.

$$\begin{aligned} \Delta_f H_m^\circ(\text{SnCl}_2, \text{cr}) &= - (328.01 \pm 2.08) \text{kJ} \cdot \text{mol}^{-1} \text{ (recalculated value, } 2\sigma) \\ &\quad - (327.86 \pm 1.09) \text{kJ} \cdot \text{mol}^{-1} \text{ (original value)} \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr}) &= - (918.95 \pm 2.74) \text{kJ} \cdot \text{mol}^{-1} \text{ (recalculated value, } 2\sigma) \\ &\quad - (918.26 \pm 1.42) \text{kJ} \cdot \text{mol}^{-1} \text{ (original value)} \end{aligned}$$

**[1974ANI/STE]**

Anisimov *et al.* [1974ANI/STE] determined the heat capacity of cubic SnI<sub>4</sub> in the temperature range of 11.5 to 308 K on a sample of high purity with an accuracy of the measurements estimated as lying within 0.1 to 0.2 %. The values are reported in Table A-29.

Table A-29: Heat capacity data for SnI<sub>4</sub>(cr) from [1974ANI/STE].

$T/K$	$C_{p,m}^{\circ}(\text{SnI}_2, \text{cr}, T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S_m^{\circ}(\text{SnI}_2, \text{cr}, T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
11.0000	17.7234	6.1086
16.0000	33.5431	15.4766
20.0000	44.4341	24.1710
24.0000	53.4715	33.0996
30.0000	63.9734	46.2332
40.0000	75.8141	66.3582
60.0000	90.4581	100.0813
80.0000	100.6670	127.5702
100.0000	107.6962	150.8332
120.0000	112.8843	170.9164
140.0000	116.6081	188.6147
170.0000	120.8758	211.7104
200.0000	124.0974	231.5844
230.0000	126.6915	249.1154
260.0000	129.2856	264.8054
273.1500	130.3316	271.2069
298.1500	131.9634	282.7129
310.0000	132.5910	287.8592

**[1974ANI/ZHA]**

Anisimov *et al.* [1974ANI/ZHA] determined the heat capacity of SnI<sub>2</sub>(cr) (11.7 to 312.7 K) on a sample of high purity with an accuracy of the measurements estimated as lying within 0.1 to 0.2% (see Table A-30).

Table A-30: Heat capacity data for SnI<sub>2</sub>(cr) from [1974ANI/ZHA].

$T/K$	$C_{p,m}^{\circ}(\text{SnI}_2, \text{cr}, T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S_m^{\circ}(\text{SnI}_2, \text{cr}, T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
12.0000	11.0374	4.4769
16.0000	18.4556	8.6692
20.0000	24.8404	13.4892
24.0000	30.4260	18.5268
30.0000	37.1916	26.0789
40.0000	45.2709	37.9656
60.0000	55.2706	58.3668
80.0000	61.3374	75.1865
100.0000	65.3959	89.3284
120.0000	68.2410	101.5038
140.0000	70.2912	112.1730
170.0000	72.6342	126.0639
200.0000	74.3078	137.9883
230.0000	75.7304	148.4902
260.0000	76.9856	157.8623
273.1500	77.5295	162.7994
298.1500	78.4500	168.4897
310.0000	78.7847	171.5440

**[1974MES/BAE]**

The dissociation equilibria of phosphoric acid were studied potentiometrically up to 300 °C. The results indicated the absence of significant amounts of polyphosphates up to 200 °C.

**[1974MAT/OGU]**

Matsuo *et al.* [1974MAT/OGU] measured calorimetrically the heat capacity of SnCl<sub>2</sub>·2H<sub>2</sub>O crystals from 13 to 300 K. The solid of high purity was prepared from a slowly cooled melt with a nearly stoichiometric content of water. The overall accuracy of the measurement is estimated as 1% at 20 K and less than 0.3% above 50 K. The data are shown in Table A-31.

Table A-31: Heat capacity of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  from [1974MAT/OGU].

$T/\text{K}$	$C_{p,m}^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
79.53	72.58	140.63	107.10	223.59	145.91	149.51	112.73
82.57	74.91	142.85	108.19	224.99	145.39	151.79	115.14
85.19	76.80			227.01	145.06	154.04	116.93
87.38	78.41	142.05	107.67	229.23	145.06	156.28	117.43
89.46	79.75	144.54	108.77			158.50	117.51
91.26	80.81	147.28	109.95	79.49	72.46	160.71	118.54
93.28	82.15	149.98	111.08	81.62	74.05	162.91	119.26
95.26	83.31	152.66	111.64	84.93	76.47	165.09	120.28
98.02	85.00	155.31	113.55	89.00	79.31	167.26	121.15
99.92	86.15	157.90	115.77				
101.81	87.23	160.45	117.45	109.97	91.65	172.27	123.70
103.66	88.32	162.97	119.24	112.65	93.04	174.79	124.57
105.49	89.37	165.49	120.75	116.97	95.84	177.35	125.23
107.30	90.37	167.99	121.85	119.78	96.74	179.94	126.82
109.10	91.39	170.47	122.94	122.54	98.30	182.50	127.95
110.87	92.30			125.27	99.55	185.05	129.07
		299.72	166.86	127.96	100.89	187.59	130.08
11.70	3.85	301.18	168.54	130.61	102.16	190.10	131.28
12.60	4.49			133.23	103.40	192.60	132.44
13.67	5.46	153.82	112.55	136.37	104.85	195.07	133.58
14.82	6.68	155.06	112.95	138.92	105.91	197.53	134.67
15.99	7.69	156.29	114.29	141.25	107.13	199.96	135.94
17.23	9.19	157.49	116.42	143.95	108.19		
18.39	10.45	158.69	117.60	146.43	109.34	228.35	145.00
19.46	11.72	159.85	118.46	148.89	110.72	230.76	145.10
20.72	13.12	161.27	118.19			233.17	145.42
22.07	14.80	162.40	119.30	213.92	145.84	235.55	145.78
23.36	16.26			215.34	148.49	237.93	146.38
24.61	17.60	182.53	127.88	215.59	149.07	240.28	146.88
26.08	19.50	183.59	128.64	215.82	149.62	242.62	147.33
27.72	21.48			216.04	150.27	244.95	147.70
29.34	23.40	267.71	154.33	216.26	151.34	247.26	148.92
30.94	25.34	270.11	154.84	216.48	152.13		
32.42	27.06	272.49	155.68	216.74	153.92	249.58	148.87
33.79	28.71	274.89	156.82	216.99	155.83	252.01	149.52
35.22	30.45	277.25	157.38	217.21	158.02	254.44	150.22

(Continued on next page)

Table A-31 (continued)

$T/K$	$C_{p,m}^{\circ} /$ $J \cdot mol^{-1} \cdot K^{-1}$	$T/K$	$C_{p,m}^{\circ} /$ $J \cdot mol^{-1} \cdot K^{-1}$	$T/K$	$C_{p,m}^{\circ} /$ $J \cdot mol^{-1} \cdot K^{-1}$	$T/K$	$C_{p,m}^{\circ} /$ $J \cdot mol^{-1} \cdot K^{-1}$
36.72	32.23	279.62	157.99	217.42	162.79	256.85	150.93
38.46	34.22	281.96	158.89	217.63	168.80	259.25	151.75
40.42	36.38	284.31	159.85	217.82	210.90	261.64	152.56
42.24	38.41	286.63	161.09	217.94	251.25	264.03	153.15
43.96	40.27	288.94	161.89	218.07	181.05	266.41	153.80
45.76	42.22	291.25	162.66	218.27	166.20	268.78	154.43
47.65	44.28	293.54	163.74	218.48	159.55		
49.45	46.09			218.69	156.92	135.79	104.01
51.32	48.15	203.38	137.71	218.91	154.88	137.51	105.03
53.27	50.04	205.49	138.92	219.13	153.97	140.32	106.56
55.14	51.79	208.62	140.90	219.35	151.86		
56.93	53.48	211.93	143.44	219.57	151.45	135.91	104.61
58.84	55.39	213.7628	145.70	219.79	150.00	138.07	105.70
61.20	57.61	214.6714	146.95	220.01	149.15	140.22	106.84
63.79	60.00	215.2727	148.32	220.31	149.20	141.81	107.46
66.26	62.11	215.8690	149.66	220.72	148.04	143.40	108.10
68.64	64.08	215.4597	152.27	221.25	147.51	144.73	108.67
70.94	65.91	217.0417	156.35	221.90	146.91	145.73	107.83
73.18	67.62	217.5987	171.73	222.78	146.11	146.84	109.67
75.35	69.36	218.0552	171.79	224.02	145.59	147.89	110.12
77.46	71.00	219.1017	153.29	225.44	145.24	148.95	110.49
		219.500	150.8	226.86	145.01	150.00	111.02
129.95	102.15	220.100	149.11	228.29	144.93	151.30	111.20
131.91	103.03	220.650	148.21			152.85	112.15
133.86	104.01	221.4777	147.00	142.42	107.62	155.13	112.66
136.14	105.01	222.0787	146.64	144.81	108.68	156.12	115.60
138.39	105.73	222.6813	146.06	147.18	109.94	165.84	119.63

**[1974MIL]**

A good review and critical evaluation of the experimental data on thermodynamic properties of tin sulfides to 1974. Properties include: structure, melting and transition quantities, standard entropy, standard enthalpy of formation, heat capacity, dissociation energy, dissociation pressure and vapour pressure. Auxiliary data used in deriving standard properties from measurements at other temperatures are explicitly stated (*i.e.*, heat capacity, entropy, enthalpy of fusion and transition of pertinent elements).

**[1974POU]**

Pourbaix's data on  $\Delta_f G_m^\circ(\text{Sn}^{2+})$  and  $\Delta_f G_m^\circ(\text{Sn}^{4+})$  were taken from [1952LAT] and supplied in these cases no additional information.

**[1975DAV/DON]**

Tritin(II) dihydroxide oxide sulfate,  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ , was prepared by slow hydrolysis of tin(II) sulfamate. Crystals so obtained were better for structure determination but otherwise identical in every respect to the basic sulfate precipitated from aqueous solution [1967DAV/DON]. The crystal structure of this compound was determined from X-ray diffractometer data by Patterson and Fourier methods. Crystals are orthorhombic and piezoelectric, space group  $Pbc2_1$  with  $Z = 4$  in a unit cell of dimensions  $a = (4.983 \pm 0.002) \text{ \AA}$ ,  $b = (13.128 \pm 0.005) \text{ \AA}$ ,  $c = (12.214 \pm 0.005) \text{ \AA}$ . The structure was refined by least-squares methods to  $R$  0.028 for 1070 reflections. The structure contains discrete ring  $[\text{Sn}_3\text{O}(\text{OH})_3]^{2+}$  basic ions which have Sn in two different environments: one Sn is bonded to all three ring oxygens to give trigonal pyramidal co-ordination with short Sn–O, and the remaining Sn atoms are bonded to two ring O atoms with short Sn–O ( $< 2.16 \text{ \AA}$ ), and has O atoms from separate  $\text{SO}_4$  groups at longer ( $> 2.40 \text{ \AA}$ ) distances. These latter Sn atoms have distorted square-pyramidal oxygen environments.

**[1975DEM/KOS]**

The calorimetric data on the arsenides measured over the temperature range 55 to 310 K were used to calculate the standard thermochemical data; these data have been rediscussed by Koshchenko *et al.* [1980KOS/DEM] extending the calculations to 5 K.

**[1975FED/BOL]**

Potentiometric measurements using a tin amalgam electrode have been performed to study the formation of the binary chlorido and bromido, as well as the ternary chlorido-bromido complexes of tin(II) at 25 °C in  $\text{NaClO}_4$  media ( $I = 0.5, 1.0, 3.0, 4.0$  and  $6.0 \text{ M}$ ). The formation constants of the binary bromido complexes for  $I = 0.5$  were determined in [1975FED/BOL], while for the other ionic strength they were taken from [1969FED/BOL]. The authors concluded the formation of three binary chlorido species ( $\text{SnCl}_q^{2-q}$ ,  $q = 1, 2, 3$ ) and four ternary complexes ( $\text{SnCl}_x\text{Br}_y^{2-x-y}$ ,  $(x,y) = (1,1), (1,2), (2,1)$  and  $(1,3)$ ). A slightly modified form of the Vasil'ev equation has been applied to calculate the thermodynamic formation constants. The graphical presentation of the experimental data are provided only for  $I = 3 \text{ M}$ . Based on this information, *c.a.* 40% of the original ionic medium was substituted by  $\text{NaCl}/\text{NaBr}$  for the investigations of the binary complexes, while the  $\text{NaClO}_4$  medium was entirely replaced during the measurements of the ternary complexes. Therefore, an uncertainty of  $\pm 0.4$  has been assigned to the  $\log_{10} \beta_q$  values of the binary complexes, while the formation constants of the ternary complexes were not considered any further in this review.



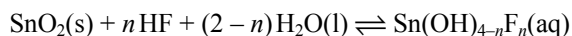
**[1975GRI]**

The crystal structure of tritin(II) dihydroxide oxide sulfate,  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ , was determined. The compound crystallises in the orthorhombic system with  $a = (13.045 \pm 0.002) \text{ \AA}$ ,  $b = (4.9383 \pm 0.0014) \text{ \AA}$ ,  $c = (12.140 \pm 0.002) \text{ \AA}$ . The space group is  $Pca2_1$ . There are four formula units in the unit cell.

The positions of the tin, sulfur, and oxygen atoms were obtained from Patterson and Fourier syntheses. Full matrix least-squares refinement, based on 452 independent reflections, gave a final  $R$ -value of 6.9%. The tin and oxygen atoms form infinite chains connected by distorted sulfate groups. Two tin atoms are four-coordinated by oxygen while the third is three-coordinated. The Sn–O bonding distances vary within the range 2.01 – 2.51 Å with a standard deviation of 0.003 Å. The shortest tin – tin distances are 3.523, 3.578, and 3.580 Å with a mean standard deviation of 0.004 Å.

**[1975KLI/BAR]**

The solubility of amorphous  $\text{SnO}_2$  in acidic and alkaline fluoride solutions has been studied at 25, 50 and 200 °C. The equilibration time was 30 days at 25 °C, 7 days at 200 °C. The dissolved tin(IV) in the equilibrated solutions was determined colorimetrically using phenylfluorone. In acidic solution the formation of  $\text{Sn}(\text{OH})_3\text{F}(\text{aq})$  was suggested at 25 and 50 °C, while  $\text{Sn}(\text{OH})_2\text{F}_2(\text{aq})$  was suggested at 200 °C. In alkaline fluoride solutions the predominant complex was found to be  $\text{Sn}(\text{OH})_4\text{F}^-$  at 25 and 50 °C, and  $\text{Sn}(\text{OH})_4\text{F}_2^{2-}$  at 200 °C. For the reactions



$\log_{10} {}^*K^{\circ} = -(5.0 \pm 0.2)$  (25 °C,  $n = 1$ ),  $-(4.4 \pm 0.1)$  (50 °C,  $n = 1$ ) and  $-(3.5 \pm 0.2)$  (200 °C,  $n = 2$ ) has been reported.

In alkaline solutions  $\log_{10} {}^*K^{\circ} = -(5.4 \pm 0.1)$  (25 °C,  $n = 1$ ),  $-(5.8 \pm 0.2)$  (50 °C,  $n = 1$ ) and  $-(3.8 \pm 0.2)$  (200 °C,  $n = 2$ ) has been reported for the reaction  $\text{SnO}_2(\text{s}) + n\text{F}^- + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Sn}(\text{OH})_4\text{F}_n^{n-}$ .

Although the experimental work seems to have been done carefully, there are several deficiencies in this work: (i) the accuracy of the analytical method used is rather limited at  $[\text{Sn}(\text{IV})]_{\text{tot}} = 10^{-7} - 10^{-6} \text{ M}$ , (ii) the compositions of the dissolved mixed complexes are not certain (e.g. the formation of  $\text{Sn}(\text{OH})_2\text{F}^+$  or  $\text{Sn}(\text{OH})_5\text{F}_2^{2-}$  is also possible), (iii) the formation of the binary hydroxido complexes, e.g.  $\text{Sn}(\text{OH})_3^+$  at pH = 1 or  $\text{Sn}(\text{OH})_5^-$  at pH = 10, was not considered (iv) the pH of the solutions was calculated and not measured. Therefore, the reported constants cannot be used to derive selected values.

**[1975MIK/JAN2]**

Mikler and Janitsch measured the heat of reaction  $\text{SnI}_2(\text{s}) + \text{I}_2(\text{s}) + 4045 \text{CS}_2(\text{l}) \rightleftharpoons [\text{SnI}_4; 4045 \text{CS}_2](\text{sol})$  to be  $-(41.12 \pm 0.55) \text{ kJ}\cdot\text{mol}^{-1}$  by isoperibol solution calorimetry. The heat of formation of  $\text{SnI}_2(\text{s})$  was calculated by using the literature data for  $\text{SnI}_4(\text{s})$  previously measured by Mikler [1973MIK]. The obtained value of the enthalpy of formation at 298.15 K for  $\text{SnI}_2(\text{s})$  is  $-(153.9 \pm 1.40) \text{ kJ}\cdot\text{mol}^{-1}$ .

The calorimetric study provides good reliable data on the two iodides and has been used in this review.

**[1975NEL/AMI]**

The stability constants of Sn(II) fluoride complexes were determined by potentiostatic titration at 25 °C in 0.0333 M  $\text{NaSO}_4$  solution. The solutions were prepared and stored under nitrogen atmosphere. The method involved incremental additions of fluoride ion which was followed by titration with tin(II) such that the potential difference developed between the fluoride selective and the reference electrodes remained constant. Although the method used by the authors would allow very accurate measurements. Indeed, the sulfate medium cannot be regarded as an inert electrolyte. Therefore, the reported constants were not considered any further in this review.

**[1975WAD/ITO]**

The formation constants of tin(II)-sulfate complexes were determined by measuring the potential of the cell  $\text{Sn-Hg}|\text{Sn}(\text{ClO}_4)_2, \text{NaClO}_4, \text{HClO}_4, \text{H}_2\text{SO}_4||\text{NaClO}_4||\text{SCE}$  at various ionic strengths ( $I = 0.037$  to 1.0 M) in aqueous solutions at different temperatures between 15 and 45 °C. Beside the  $\text{SnSO}_4(\text{aq})$  complex, the authors mentioned the possibility of the formation of  $\text{Sn}(\text{HSO}_4)^+$  species, too. The authors evaluated their experimental data –using the Debye-Hückel equation– assuming both the presence and absence of  $\text{Sn}(\text{HSO}_4)^+$  species. The reported formation constants were re-evaluated for the purposes of this review using the SIT. Admitting the formation of  $\text{Sn}(\text{HSO}_4)^+$  species, an unreliably high  $\Delta\varepsilon$  value ( $0.85 \text{ kg}\cdot\text{mol}^{-1}$ ) can be calculated for the reaction  $\text{Sn}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{Sn}(\text{HSO}_4)^+$ , therefore the reviewers rejected the formation of this species.

Assuming that  $\text{SnSO}_4(\text{aq})$  has been formed solely, the SIT treatment (see Figure IX-2) resulted in  $\log_{10} \beta_1^0((\text{IX.8}), 298.15 \text{ K}) = (3.43 \pm 0.25)$ ,  $\Delta\varepsilon(\text{IX.8}) = (0.11 \pm 0.33) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{SnSO}_4(\text{aq}), \text{NaClO}_4(\text{aq})) = (0.19 \pm 0.35) \text{ kg}\cdot\text{mol}^{-1}$ .

Based on the temperature dependence of complex formation processes at  $I = 0.5 \text{ M}$ , the authors reported  $\Delta_r H_m^0 = 16.9 \text{ kJ}\cdot\text{mol}^{-1}$  for the reaction  $\text{Sn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{SnSO}_4(\text{aq})$ .

**[1976BAE/MES]**

In this book the hydrolysis of cations is treated comprehensively. It has been shown that the constants of reaction



$\log_{10} K_{11}$  increase nearly linearly with the ratio of the cation charge to the M–O interatomic distance  $d$ . This was useful to estimate roughly the first hydrolysis constant of  $Sn^{4+}$ (aq).

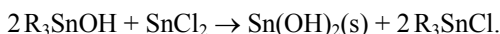
**[1976GOB]**

The hydrolysis of Sn(II) has been studied at low tin(II) concentrations by a potentiometric method using two sensors (glass and tin-amalgam electrodes) at 25 °C and  $I = 3$  M  $NaClO_4$  ( $[Sn^{2+}]_{tot} = 0.02$  to 2.3 mM). The evaluation of the experimental data indicated the formation of  $Sn_3(OH)_4^{2+}$  and  $Sn(OH)^+$ .

This is an extension of the study [1958TOB] to a lower concentration range of  $[Sn^{2+}]_{tot}$ , performed with similar accuracy. The reported experimental data were combined with those of [1958TOB] and re-evaluated for the purposes of this review. The re-evaluation confirmed the suggested speciation (see also the comment on [1958TOB]).

**[1976HON/ZUC]**

Tin(II) hydroxide has been synthesised by an anhydrous, organometallic method involving the exchange of groups between a triorganotin hydroxide and tin(II) chloride:



$Sn(OH)_2(s)$  is a white, infusible, amorphous solid. The micro-analytically determined composition was Sn 77.64% (theor.77.73%), H 1.28% (theor.1.32%). Tin(II) hydroxide is soluble in acid and alkali, gives an ambient temperature Mössbauer spectrum ( $IS = 2.78$ ,  $QS = 2.20$  mm·s<sup>-1</sup>), loses water in two stages at 126 and 195 °C to give an orange residue containing both tin(II) and tin(IV), exhibits an infrared spectrum containing  $\nu(Sn-O)$  at 575 and 340 cm<sup>-1</sup> and  $\nu(Sn-OH)$  at 3390 cm<sup>-1</sup>, and reacts with catechol to give o-phenylenedioxytin(II).

**[1976SAM/LYA]**

Potentiometric measurements using a tin amalgam electrode have been performed to study the formation of tin(II)-halogeno ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ) complexes in 1 M  $LiClO_4$  and the tin(II)-thiocyanato complexes in 1 M  $NaClO_4$  media at 25 °C in four different solvents ( $H_2O$ , MeOH, EtOH and DMF). In protic solvents the formation constants decrease in the following order:  $SCN^- \sim Cl^- > Br^- > I^-$ . The aprotic solvents have a clearly defined differentiating effect on complex stabilities. Apparently the authors took no special precaution to prevent the oxidation and the hydrolysis of tin(II) during the

measurements. No information is provided concerning the composition of the solutions, therefore a substantial replacement of the background electrolyte can be suspected. Considering these deficiencies, the reported formation constants were not considered any further in this review.

### [1976SCH/CRO]

Potentiometric measurements using fluoride selective electrode have been performed to determine the formation constants of the  $\text{SnF}_q^{2-q}$  ( $q = 1$  to 3) complexes at 25 °C in 3.0  $\text{NaClO}_4$  medium, taking special care to exclude the formation of  $\text{Sn(IV)}$ . The experiments were performed in acidic solutions ( $\text{pH} = 1.3 - 1.6$ ) to prevent the hydrolysis of tin(II) and the formation of  $\text{HF}$  and  $\text{HF}_2^-$  was taken into account. The experiments were performed carefully. The equilibrium constants for the reactions  $\text{H}^+ + \text{F}^- \rightleftharpoons \text{HF}$  ( $\log_{10} K = 3.33$ ) and  $\text{HF} + \text{F}^- \rightleftharpoons \text{HF}_2^-$  ( $\log_{10} K = 0.94$ ) were taken from [1970KLE]. The graphical presentations indicate good fit to the experimental data.

### [1976SHA]

This paper contains the most reliable list of effective ionic radii for metal ions. The nature of  $\text{Sn}^{2+}$ , however, made it impossible to define its ionic radius. The coordination of  $\text{Sn}^{2+}$  by oxygen or fluorine is always extremely irregular, leading to average distances which depend on the degree of distortion. As this distortion varies widely from one compound to another, it is not meaningful to define an ionic radius. Thus entropy, charge, ionic radii correlations do not lead to sufficiently accurate predictions of  $S_m^\circ$  ( $\text{Sn}^{2+}$ , 298.15 K).

With  $\text{Sn}^{4+}$  the situation is quite different, in Table A-32 the effective ionic radii of tin(IV) ion depending on coordination numbers are listed. For the entropy, charge, ionic radii correlation of VI coordinated  $\text{Sn}^{4+}$  the value of 0.69 Å should be used.

Table A-32: Effective ionic radii of  $\text{Sn}^{4+}$ .

Ion	Electronic configuration	Coordination Number	C.R. <sup>(a)</sup> /Å	'IR' <sup>(b)</sup> /Å	
$\text{Sn}^{4+}$	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	IV	0.69	0.55	R <sup>(c)</sup>
		V	0.76	0.62	C <sup>(d)</sup>
		VI	0.83	0.69	R <sup>(e)</sup>
		VII	0.89	0.75	
		VIII	0.95	0.81	C <sup>(d)</sup>

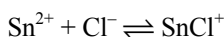
(a): crystallographic radius; (b): 'IR' effective ionic radius ; (c): R from  $r^3$  vs.  $V$  plots, (d): C = calculated, (e): most reliable.

**[1976VAS/GLA]**

The cell potential of Pt(H<sub>2</sub>)|HCl|AgCl, Ag, and that of Pt(H<sub>2</sub>)|HCl, HClO<sub>4</sub>|AgCl, Ag was determined under various concentrations and temperature conditions. With constant ionic strength of the electrolyte the effective standard potential of the AgCl|Ag electrode was stable. Values of the cell potentials estimated at constant ionic strength permit evaluating the potential determining concentrations of this system. Extrapolation of data to zero ionic strength can be used for the determination of thermodynamic properties of the solution. The activity coefficients of HCl in aqueous solution and in the presence of HClO<sub>4</sub> were evaluated.

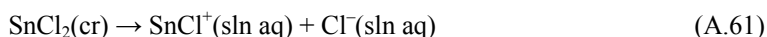
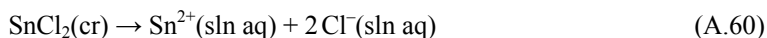
**[1976VAS/KOK]**

The thermodynamic characteristics of Sn<sup>2+</sup> and SnCl<sup>+</sup> ions and the thermodynamics of the process



at various temperatures and ionic strengths of the solution have been calculated from measurements of the heat of dissolution of SnCl<sub>2</sub>(cr) and SnCl<sub>2</sub>·2H<sub>2</sub>O(cr) at 10 and 25 °C in 0.2 to 3.0 M HClO<sub>4</sub> solutions.

This is a key paper for the evaluation of  $\Delta_f H_m^{\circ}(\text{Sn}^{2+}, 298.15 \text{ K})$ . The experimental results at 10 °C are given only graphically and those at 25 °C are given in [1973VAS/VAS]. The dissolution of SnCl<sub>2</sub>(cr) in HClO<sub>4</sub> solutions can be represented by the following equations:



The equations for dissolution of SnCl<sub>2</sub>·2H<sub>2</sub>O(cr) are analogous. Eqs.(A.60) to (A.62) contribute to the measured value  $\Delta_{\text{diss}} H$ .

$$\Delta_{\text{diss}} H = \alpha_1 \Delta H (\text{A.60}) + \alpha_2 \Delta H (\text{A.61}) + \alpha_3 \Delta H (\text{A.62}).$$

Where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are the fractions of Sn<sup>2+</sup>, SnCl<sup>+</sup> and SnCl<sub>2</sub>;  $\Delta H (\text{A.60})$ ,  $\Delta H (\text{A.61})$  and  $\Delta H (\text{A.62})$  are the enthalpy contributions of Reactions (A.60), (A.61) and (A.62). For the calculation of  $\alpha_n$  the authors used the stability constants of Table A-33, which were estimated on the basis of experimental data in [1952VAN/RHO] and [1961TOB/HUG].

Recalculation with a set of constants, selected by the reviewers, will in principle be possible only when the composition of the solutions used for calorimetry can be ascertained. This is the case in [1973VAS/VAS], but not in this paper. Consequently the recalculation was based on the data listed in Table A-33 for 25 °C [1976VAS/KOK].

Table A-33: Stability constants of tin(II) chlorido-complexes,  $\log_{10} \beta_q$ .

$t / ^\circ\text{C}$	$I/M (\text{HClO}_4)$	$\text{SnCl}^+$	$\text{SnCl}_2$	$\text{SnCl}_3^-$
10	0.0	$1.51 \pm 0.01$	$2.20 \pm 0.02$	$1.18 \pm 0.04$
10	0.2	0.98	1.40	0.38
10	0.5	0.89	1.26	0.24
10	1.0	0.90	1.30	0.58
10	2.0	0.95	1.41	0.99
10	3.0	1.05	1.58	1.46
25	0.0	$1.04 \pm 0.01$	$2.43 \pm 0.12$	$1.40 \pm 0.01$
25	0.5	1.00	1.47	0.44
25	1.0	1.01	1.51	0.78
25	2.0	1.06	1.61	1.18
25	3.0	1.16	1.79	1.66

In the course of recalculation the methods proposed by [1997ALL/BAN] p. 412 and [1967VAS], [1978VAS/YAS] were compared. As Figure A-37 to Figure A-40 show the differences in the extrapolated  $\Delta_f H_m^\circ$  values are small but noticeable. For the final calculation of  $\Delta_f H_m^\circ (\text{Sn}^{2+}, 298.15 \text{ K})$  the results of [1973VAS/VAS2] and [1976VAS/KOK] have to be combined with  $\Delta_f H_m^\circ (\text{Cl}^-, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ (\text{H}_2\text{O}, 1, 298.15 \text{ K})$  of [1989COX/WAG].

The exclusion of dioxygen is not reported, although it can be assumed considering the scientific competence of the authors. The data reported in [1973VAS/VAS] and [1976VAS/KOK] have been used to calculate the standard enthalpies of formation of  $\text{Sn}^{2+}$  and  $\text{SnCl}^+$  ions, as well as the enthalpy of the reaction  $\text{Sn}^{2+} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$ . The graphically presented experimental data in [1973VAS/VAS] for  $25^\circ\text{C}$  were re-evaluated for the purpose of this review. Using the selected  $\log_{10} \beta_q^\circ$  ((A.63),  $q = 1, 2, 3, 298.15 \text{ K}$ ) and  $\Delta \alpha$ ((A.63),  $q = 1, 2, 3$ ) values, as well as the assumptions that  $\alpha(\text{SnCl}_2, \text{NaClO}_4) = \alpha(\text{SnCl}_2, \text{HClO}_4)$  and  $\alpha(\text{Na}^+, \text{SnCl}_3^-) = \alpha(\text{H}^+, \text{SnCl}_3^-)$ , the formation constants of the species  $\text{SnCl}_q^{2-q}$  ( $q = 1, 2, 3$ ) in perchloric acid solutions according to the reaction:



can be estimated (Table A-34).

Figure A-37: Determination of the enthalpy of dissolution of  $\text{SnCl}_2(\text{cr})$  according to the reaction  $\text{SnCl}_2(\text{cr}) \rightleftharpoons \text{Sn}^{2+} + 2 \text{Cl}^-$  in  $\text{HClO}_4$  medium at  $25^\circ\text{C}$ . Extrapolation to infinite dilution according to [1967VAS]. (●: experimental data of [1976VAS/KOK]; solid line: linear fit; dotted lines: 95% confidence limits).

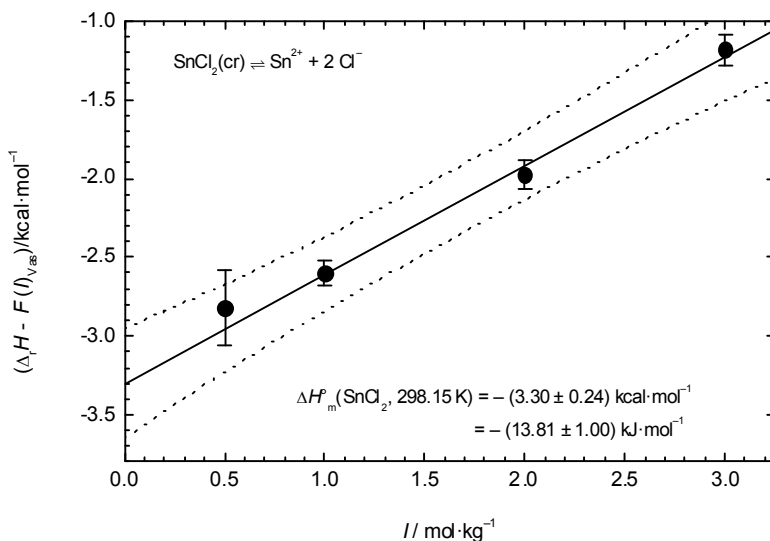


Figure A-38: Determination of the enthalpy of dissolution of  $\text{SnCl}_2(\text{cr})$  according to the reaction  $\text{SnCl}_2(\text{cr}) \rightleftharpoons \text{Sn}^{2+} + 2 \text{Cl}^-$  in  $\text{HClO}_4$  medium at  $25^\circ\text{C}$ . Extrapolation to infinite dilution according to [1997ALL/BAN] (Eq. IX.72,  $r = 0$ ). (●: experimental data of [1976VAS/KOK]; solid line: linear fit; dotted lines: 95% confidence limits).

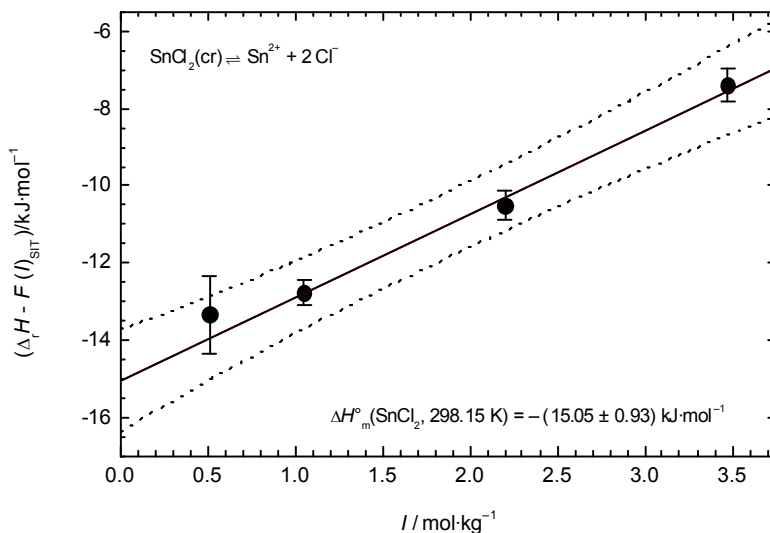


Figure A-39: Determination of the enthalpy of dissolution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  according to the reaction  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Sn}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O}(\text{l})$  in  $\text{HClO}_4$  medium at  $25^\circ\text{C}$ . Extrapolation to infinite dilution according to [1967VAS] (●: experimental data of [1976VAS/KOK]; solid line: linear fit; dotted lines: 95% confidence limits).

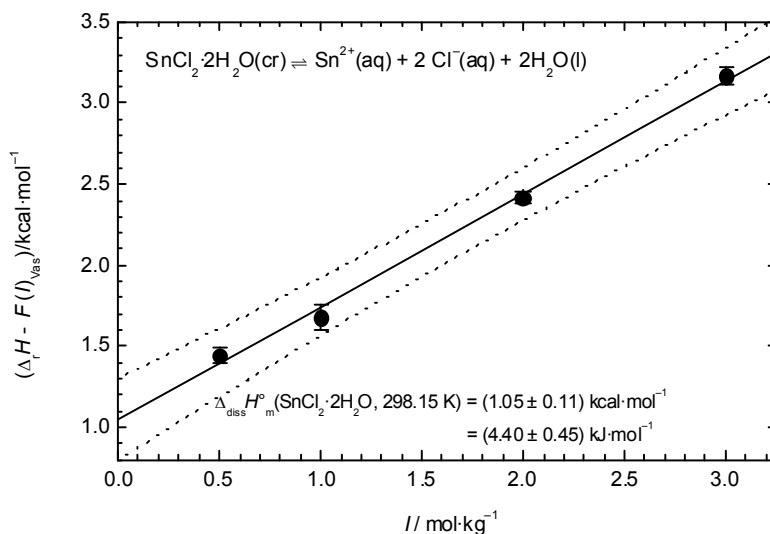


Figure A-40: Determination of the enthalpy of dissolution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  according to the reaction  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Sn}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O}(\text{l})$  in  $\text{HClO}_4$  medium at  $25^\circ\text{C}$ . Extrapolation to infinite dilution according to [1997ALL/BAN] (Eq. IX.72) (●: experimental data of [1976VAS/KOK]; solid line: linear fit; dotted lines: 95% confidence limits).

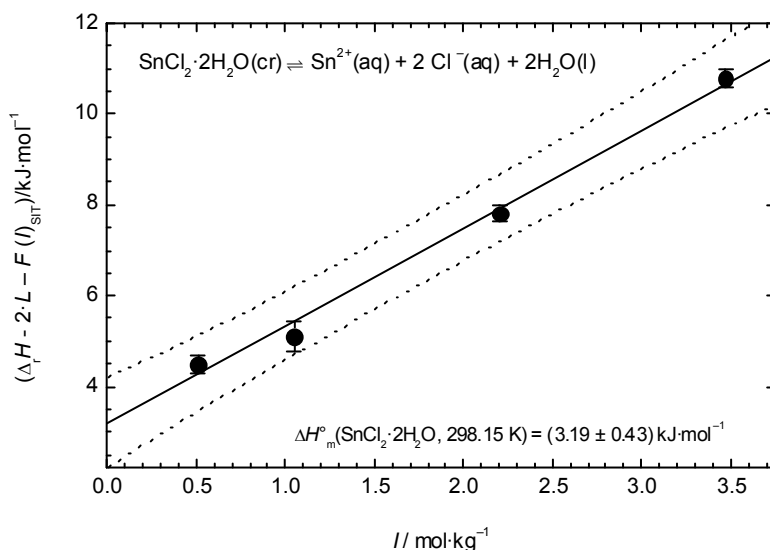
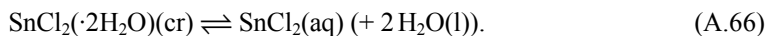
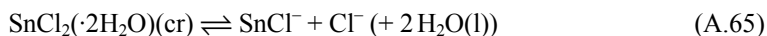
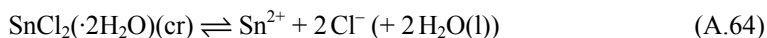




Table A-34: Formation constants of the species  $\text{SnCl}_q^{2-q}$  ( $q = 1$  to 3) in perchloric acid media.

	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_3$
0.2 M HClO <sub>4</sub>	1.03	1.43	1.50
0.49 M HClO <sub>4</sub>	0.95	1.34	1.42
1.02 M HClO <sub>4</sub>	0.96	1.40	1.51
1.96 M HClO <sub>4</sub>	1.13	1.73	1.88
2.93 M HClO <sub>4</sub>	1.37	2.19	2.38
3.95 M HClO <sub>4</sub>	1.68	2.76	3.01

Simulations using the values listed in Table A-34 revealed, that under the conditions  $[\text{Sn}^{2+}]_{\text{tot}} < 0.1I_m$  only the species  $\text{Sn}^{2+}$ ,  $\text{SnCl}^+$  and  $\text{SnCl}_2(\text{aq})$  are present in the solutions. By calculating the speciation of tin(II) in the solutions used in [1973VAS/VAS], the measured heats of dissolution can be separated into the heats of three processes:



The calculated individual heats of the above processes are listed in Table A-35.

Table A-35: Enthalpy of Reactions (A.64), (A.65) and (A.66) in  $\text{kJ}\cdot\text{mol}^{-1}$ .

	$\text{SnCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$			$\text{SnCl}_2(\text{cr})$		
	$\Delta_r H_m$ (A.64)	$\Delta_r H_m$ (A.65)	$\Delta_r H_m$ (A.66)	$\Delta_r H_m$ (A.64)	$\Delta_r H_m$ (A.65)	$\Delta_r H_m$ (A.66)
0.2 M HClO <sub>4</sub>	$5.3 \pm 0.7$			$-13.0 \pm 0.2$		
0.49 M HClO <sub>4</sub>	$7.4 \pm 0.2$					
1.02 M HClO <sub>4</sub>	$8.7 \pm 0.5$	$17.1 \pm 1.6$	$24.4 \pm 3.0$	$-9.4 \pm 0.3$	$0.0 \pm 1.9$	$0.8 \pm 3.0$
1.96 M HClO <sub>4</sub>	$11.6 \pm 0.4$	$18.3 \pm 0.7$	$22.9 \pm 1.2$	$-6.6 \pm 0.4$	$0.7 \pm 0.9$	$3.7 \pm 2.2$
2.93 M HClO <sub>4</sub>	$14.6 \pm 0.6$	$19.9 \pm 1.0$	$24.1 \pm 1.3$	$-3.0 \pm 0.5$	$1.5 \pm 1.3$	$5.7 \pm 2.8$
3.95 M HClO <sub>4</sub>	$19.4 \pm 0.4$	$22.6 \pm 0.8$	$23.8 \pm 1.4$			

The above enthalpy values were used to calculate the heats of the following reactions:



$$\Delta_r H_m (\text{A.67}) = \Delta_r H_m (\text{A.65}) - \Delta_r H_m (\text{A.64})$$

and  $\Delta_r H_m$  (A.68) =  $\Delta_r H_m$  (A.66) –  $\Delta_r H_m$  (A.64).

The average values of  $\Delta_r H_m$  (A.67) and  $\Delta_r H_m$  (A.68), calculated from the data obtained for both SnCl<sub>2</sub>·2H<sub>2</sub>O(cr) and SnCl<sub>2</sub>(cr), are listed in Table VIII-10 of Chapter VIII.

The enthalpy values listed in Table A-35 were extrapolated to zero ionic strength using the SIT. The standard enthalpy of Reactions (A.64) to (A.66) and the corresponding  $\Delta \varepsilon_L$  values are collected in Table A-36.

Table A-36: The standard enthalpy of Reactions (A.64) to (A.66). The values were extrapolated using the SIT and the data of Table A-35.

	SnCl <sub>2</sub> ·2H <sub>2</sub> O(cr)			SnCl <sub>2</sub> (cr)		
	(A.64)	(A.65)	(A.66)	(A.64)	(A.65)	(A.66)
$\Delta_r H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	3.01 ± 0.14	13.8 ± 1.2	22.9 ± 2.1	-15.83 ± 0.20	-1.8 ± 2.3	-1.2 ± 4.2
$10^3 \Delta \varepsilon_L / \text{kg K}^{-1} \text{mol}^{-1}$	3.17 ± 0.12	2.0 ± 0.5	0.3 ± 0.9	3.34 ± 0.20	0.7 ± 1.2	2.9 ± 2.4

### [1977MAR2]

The complex formation between tin(II) and hydroxide ion has been studied in strongly alkaline solution (pH ≥ 13) by a potentiometric method using a tin-amalgam electrode at 25 °C and  $I = 3 \text{ M NaClO}_4$  ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.25 \text{ to } 1.0 \text{ mM}$ ).

The experiments were performed at very high pH where the formation of Sn(OH)<sub>3</sub><sup>-</sup> is complete. Nevertheless, the author claimed to determine the free tin(II) concentration using the tin-amalgam electrode ( $E(\text{Sn}^{2+}/\text{Sn}(0)) = E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) + (RT/2F) \ln ([\text{Sn}^{2+}]) + E_j$ , where  $E_j$  is the liquid junction potential). Therefore, somewhat surprising values are listed in Table 2, e.g.  $\log_{10} ([\text{Sn}^{2+}]_{\text{tot}}/[\text{Sn}^{2+}]_{\text{free}}) = 22.83$ , which corresponds to  $[\text{Sn}^{2+}]_{\text{free}} = 1.5 \times 10^{-26} \text{ M}$  (i.e. one tin(II) ion exists in 100 liters of solution). Obviously, under the conditions used the electrode reaction is  $\text{Sn}(\text{OH})_3^- + 2e^- \rightleftharpoons \text{Sn}(s) + 3\text{OH}^-$ , i.e. the potential is defined by  $E(\text{Sn}(\text{OH})_3^-/\text{Sn}) = E^\circ(\text{Sn}(\text{OH})_3^-/\text{Sn}) + (RT/2F) \ln ([\text{Sn}(\text{OH})_3^-]/[\text{OH}^-]^3)$ . The equation  $E(\text{Sn}^{2+}/\text{Sn}) = E^\circ(\text{Sn}^{2+}/\text{Sn}(0)) + (RT/2F) \ln ([\text{Sn}^{2+}])$  has no physical meaning under the conditions used. Nevertheless, the data can be used for a mathematical treatment. The experimental work was done carefully, therefore the reported formation constant ( $\text{Sn}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Sn}(\text{OH})_3^-$ ,  $\log_{10} \beta_3 = (24.58 \pm 0.04)$ ) is considered in this review.

To test whether Sn(OH)<sub>2</sub>(aq) is present at low hydroxide concentrations the solubility data in alkaline and acid solutions obtained by [1941GAR/HEI] were used. The solubility product,  $K_{s,0}$ , was calculated for SnO(s) dissolved in alkaline solutions, assuming that only Sn(OH)<sub>3</sub><sup>-</sup> is present even at very low hydroxide concentrations. The complex formation constants reported by [1958TOB] were used for the same

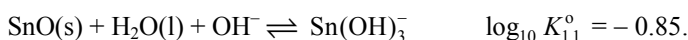
calculations in acid solutions. The mean values thus obtained (molarity basis,  $I = 3.0$  M (Na)ClO<sub>4</sub>, 25 °C) were:



$$\log_{10} K_{s,0}(\text{A.69}) = -25.43 \text{ (SnO(s) dissolved in hydroxide)}$$

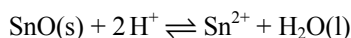
$$\log_{10} K_{s,0}(\text{A.69}) = -25.4 \text{ (SnO(s) dissolved in acid).}$$

The value for SnO(s) dissolved in hydroxide has been obtained by combining Mark's ( $I = 3.0$  M (Na)ClO<sub>4</sub>) and Garret and Heiks' ( $I = 0$ ) results for 25 °C [1941GAR/HEI]:



As Garret and Heiks' dissolution reaction is isoelectronic, the ionic strength correction is probably small and can be neglected indeed.

The value designated by SnO(s) dissolved in acid, has been recalculated using the re-evaluation of [1941GAR/HEI] by this review:



$$\log_{10} {}^*K_{s,0}^0(\text{m}) = \log_{10} {}^*K_{s,0}(\text{m}) - 2D + \log_{10} a_{\text{H}_2\text{O}} + \{\varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-)\} \cdot m(\text{ClO}_4^-)$$

$$\log_{10} {}^*K_{s,0}^0(\text{M}) = \log_{10} {}^*K_{s,0}(\text{m}) + \log_{10} \xi$$

$$\log_{10} {}^*K_{s,0}^0(\text{M}) = 2.00 + 0.5004 + 0.0535 + 0.3163 + 0.0674 = 2.94.$$

Combining this value with the ionic product of water at  $I = 3.0$  M (Na)ClO<sub>4</sub>,  $\log_{10} K_w = -14.22$  [1957ING/LAG] results in  $\log_{10} K_{s,0} = -25.50$  in reasonable agreement with Mark's estimation.

### [1977SMI/KRA]

The potential of a tin-amalgam electrode as a function of tin(II) and hydroxide ion concentration has been determined at 298 K in 3 M NaClO<sub>4</sub> medium. Since between  $[\text{OH}^-] = 0.02$  and 1 M only the species  $\text{Sn(OH)}_3^-$  exists in the solution, the electrode reaction can be defined as  $\text{Sn(OH)}_3^- + 2\text{e}^- \rightleftharpoons \text{Sn(s)} + 3\text{OH}^-$ .  $E^\circ(\text{Sn(OH)}_3^-/\text{Sn}) = 0.87$  V was determined as the standard potential of this reaction. Using the literature data  $E^\circ(\text{Sn}^{2+}/\text{Sn(0)}) = -0.136$  V, the authors calculated the formation constants of  $\text{Sn(OH)}_3^-$  ( $\text{Sn}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Sn(OH)}_3^-$ ,  $\log_{10} \beta_3 = 24.8$ ). The authors observed some deviation from the linearity of the  $E(\text{Sn(OH)}_3^-/\text{Sn})$  vs.  $[\text{OH}^-]$  curve below  $[\text{OH}^-] = 0.02$  M. This was explained by the dissociation of the complex  $\text{Sn(OH)}_3^-$ . A value of  $\text{p}K_d = (1.95 \pm 0.05)$  was reported for the reaction  $\text{Sn(OH)}_3^- \rightleftharpoons \text{Sn(OH)}_2(\text{aq}) + \text{OH}^-$ .

The experimental work seems to have been done carefully, but only graphical data are presented. The reported value of  $E^\circ$  ( $\text{Sn}(\text{OH})_3^-/\text{Sn}$ ) (0.87 V) is close to that of [1978DIC/LOT] (0.88 V). Similarly, the value of  $\log_{10} \beta_3$  (24.8) is in fairly good agreement with that reported in [1977MAR2] ( $\log_{10} \beta_3 = 24.58$ ) for the same medium. From the  $\text{p}K_{\text{d}}$  value determined in [1977SMI/KRA]  $\log_{10} \beta_{2,1}^* = -5.54$  can be obtained ( $\text{p}K_{\text{w}} = 14.2$ ,  $\log_{10} \beta_{3,1}^* = \log_{10} \beta_3 - 3 \times 14.2 = -17.8$ ), which is *ca.* 2  $\log_{10}$  units higher than expected, therefore the reason of the observed deviation of the  $E$  ( $\text{Sn}(\text{OH})_3^-/\text{Sn}$ ) vs.  $[\text{OH}^-]$  curve from the linearity is very likely more complex than the authors stated.

### [1977VAS/GLA]

Potentiometric studies on cells:



indicate that in aqueous  $\text{HClO}_4$  solutions at ionic strengths 0.6 – 2.0 M,  $\text{SnCl}_4$  (15, 25, and 35 °C) and  $\text{SnCl}_6^{2-}$  (25 °C) are completely dissociated.

According to Table 1 and Table 2 of [1977VAS/GLA] practically no Sn(IV) chlorido complex formation can be observed when 0.005 to 0.01  $\text{mol}\cdot\text{dm}^{-3}$   $\text{SnCl}_4$  are dissolved in 0.6 to 2.0  $\text{mol}\cdot\text{dm}^{-3}$   $\text{HClO}_4$  at 15, 25 and 35 °C. When 0.004 to 0.006  $\text{mol}\cdot\text{dm}^{-3}$   $(\text{NH}_4)_2\text{SnCl}_6$  were dissolved in 0.6 to 2.0  $\text{mol}\cdot\text{dm}^{-3}$   $\text{HClO}_4$  at 25 °C no evidence of complex formation could be detected either. These surprising observation clearly contradicts the results of Fatouros *et al.* [1978FAT/ROU] who base their study of Sn(IV) chlorido complexes on the cell



and find the complete, considerably stable series from  $\text{SnCl}^{3+}$  to  $\text{SnCl}_6^{2-}$ .

### [1978DIC/LOT]

Potentiometric measurements have been performed to determine the nature of the stannite ion in NaOH solution ( $[\text{NaOH}] = 0.5$  to  $5.47 \text{ mol kg}^{-1}$ ). The results are best explained by the formation of  $\text{Sn}(\text{OH})_3^-$  as the only hydroxido complex present under the conditions used. The standard potential of the reaction  $\text{Sn}(\text{OH})_3^- + 2e^- \rightleftharpoons \text{Sn}(\text{s}) + 3\text{OH}^-$  has been also determined ( $E_{\text{Sn}(\text{OH})_3^-/\text{Sn}}^\circ = 0.88 \text{ V}$ ). The experiments were performed with great care. The Pitzer approach was used to determine the standard redoxpotential of the above reaction (the Pitzer parameters of  $\text{NaSn}(\text{OH})_3$  were assumed to be equal with those of  $\text{NaBrO}_3$ ). Using  $\text{p}K_{\text{w}} = 14$  at  $I = 0$  and  $\log_{10} K(\text{Sn}^{2+}/\text{Sn}(\text{cr})) = 4.63$ ,  $\log_{10} \beta_{13}^\circ = -16.88$  can be calculated from the reported standard potential [1999LOT/OCH]. This value agrees very well with that obtained by the re-evaluation of the data reported in [1941GAR/HEI].

**[1978FAT/ROU]**

For the TDB Sn review the part of this work dealing with the determination of the apparent stability constants of chlorido-stannate(IV) complexes is of primary interest.

The  $\text{Cl}^-$  concentration was measured potentiometrically using the following cell without liquid junction:



From 10 experimental data triples  $[\text{Sn(IV)}]_{\text{tot}}$ ,  $[\text{Cl}^-]_{\text{tot}}$ ,  $[\text{Cl}^-]$  the stability constants  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ,  $\beta_4$ ,  $\beta_5$  and  $\beta_6$  were calculated.

This paper seems to be the only one reporting quantitatively on the chlorido complexes of Sn(IV) prior to [2009GAJ/SIP].

In addition, the mechanism of electrochemical reduction of Sn(IV) has been studied in strongly acidic solutions, which prevent the formation of mixed hydroxido complexes that are more difficult to reduce. In 5 M  $\text{HClO}_4$ , the presence of chloride ion substantially increases the rate constant of the reduction. To clarify the role of the chlorido complexes in the reduction, the authors studied the complex formation between Sn(IV) and chloride ion in 5 M  $\text{HClO}_4$  solution, detecting the free chloride ion by the concentration cell depicted above. The authors reported the formation of six chlorido complexes,  $\text{SnCl}_q^{4-q}$  ( $q = 1$  to 6).

The reported potentiometric data were re-evaluated for the purposes of this review. Excellent fit to the experimental data was obtained, and the resulting formation constants differs only slightly from those reported by the authors.

**[1978GLA/PAS]**

Gladeshev and Pashkov [1978GLA/PAS] made measurements on electrochemical cells of the two solids and determined the enthalpy and entropy of the reactions forming the arsenides from elements (see table below).

Table A-37: Values of the enthalpy of formation and of the entropy of  $\text{SnAs}(\text{cr})$  and  $\text{Sn}_4\text{As}_3(\text{cr})$  determined by [1978GLA/PAS] from cell-potential measurements.

Compound	$\Delta_f H_m^\circ$ (298.15 K)/ $\text{kcal}\cdot\text{mol}^{-1}$	$\Delta_f S_m^\circ$ (298.15 K)/ $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	method
$\text{SnAs}(\text{cr})$	$-6.8 \pm 0.7$	$-7.8 \pm 1.8$	Electrochemical cell
$\text{Sn}_4\text{As}_3(\text{cr})$	$-22.5 \pm 2.0$	$-19.7 \pm 1.5$	Electrochemical cell

These data cannot be reconciled with the data reviewed in this review.

**[1978KOS/SAM]**

The authors performed heat capacity measurements for SnO(tetragonal) at temperatures ranging from 4.281 to 310.70 K (see Table A-38).

Table A-38: Several series of heat capacity measurements of SnO(tetragonal) from [1978KOS/SAM].

$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
4.281	0.01179	10.056	0.1901	40.004	7.5341
4.325	0.01227	10.707	0.2315	43.593	8.6393
5.266	0.02396	11.809	0.3331	46.631	9.5768
5.4	0.02827	12.295	0.4244	50.231	10.6981
6.421	0.04820	New series		54.042	11.8775
7.024	0.06295	7.312	0.07243	57.140	12.9227
7.447	0.07706	8.468	0.1155	63.610	15.5285
7.646	0.08357	12.766	0.4512	69.244	17.0310
8.742	0.1277	13.389	0.5716	71.678	17.434
9.838	0.1826	13.941	0.5709	72.524	17.8565
10.619	0.2274	14.448	0.6809	74.684	18.4731
11.218	0.2684	14.883	0.8089	77.774	19.0753
12.066	0.3199	New series		81.986	20.2531
New series		13.060	0.4845	85.964	20.5727
5.043	0.2106	13.240	0.5004	90.031	21.9451
5.7	0.03459	14.103	0.5828	93.862	22.8806
6.155	0.04314	14.996	0.7163	97.547	23.7003
6.467	0.05047	15.883	0.8263	102.875	24.7726
6.876	0.06390	18.582	1.2347	108.005	25.8287
7.158	0.07312	20.927	1.9242	112.388	26.9378
7.837	0.08932	22.980	2.5326	116.880	27.5968
7.960	0.09696	24.474	2.8882	121.250	28.6186
8.738	0.1239	25.871	3.3384	125.345	19.1432
9.121	0.1410	27.803	3.7179	129.839	29.9470
9.831	0.1759	30.395	4.4857	133.720	30.5767
141.482	31.8992	36.529	6.4475	137.918	31.2700
145.542	32.6478	194.764	39.5183	249.700	44.5450
149.548	33.1850	198.778	39.5622	254.157	45.1311

(Continued on next page)

Table A-38 (continued)

$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnO, cr, } T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
150.487	33.4975	201.833	40.2179	258.568	45.7156
153.445	33.7506	206.248	40.2693	262.970	45.8173
154.618	33.8703	210.157	40.9835	267.330	46.1717
158.891	34.5569	212.739	41.4576	270.928	46.5365
163.663	35.1770	216.740	41.7885	275.995	46.7436
165.199	35.3586	218.064	41.7254	280.258	46.7909
168.878	35.9242	220.741	42.0032	284.513	47.0633
169.868	35.9050	222.758	42.2019	298.925	47.2888
174.008	36.6175	228.622	43.0354	294.190	47.4976
179.713	37.4284	232.511	43.3621	298.343	47.7294
183.489	37.7493	236.368	43.5969	302.467	48.0181
187.599	38.6028	236.556	43.6048	306.599	48.2005
191.262	38.9083	245.656	44.1805	310.707	48.3716

In this temperature range the coefficients of

- a) an exponential power function

$$y = ax^{b/x} \quad (\text{A.70})$$

$C_{p,m}^{\circ}(\text{SnO, cr, } T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 77.816(T/\text{K})^{[-25.295(K/T)]}$  and

- b) the Gompertz function

$$y = a \exp\{-\exp[b - c \ln(x)]\} \quad (\text{A.71})$$

$C_{p,m}^{\circ}(\text{SnO, cr, } T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 85.825 \exp\{-\exp[3.5131 - 0.71245 \ln(T/\text{K})]\}$  were fitted to the data of Table A-38. Approaches a) and b) led to  $C_{p,m}^{\circ}(\text{SnO, cr}) = 47.989 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $C_{p,m}^{\circ}(\text{SnO, cr}) = 48.093 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively. A better agreement with Kostryukov *et al.*'s result was obtained from the linear regression of the data between  $262.97 \leq T/\text{K} \leq 310.71$ ,  $C_{p,m}^{\circ}(\text{SnO, cr}) = (47.756 \pm 0.076) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The entropy was calculated a) by nonlinear regression of  $C_{p,m}^{\circ}/T$  vs.  $T$ , refitting the coefficients of  $((C_{p,m}^{\circ}/T)/\text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1} = 78.528 (T/\text{K})^{[-25.519(K/T) - 1]})$  and integrating with respect to  $T$  and b) by integrating the Gompertz function of  $C_{p,m}^{\circ}$  with respect to  $\ln(T/\text{K})$ , resulting in

- a)  $S_m^{\circ}(\text{SnO, cr, } 298.15 \text{ K}) = (57.180 \pm 0.223) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and

- b)  $S_m^{\circ}(\text{SnO, cr, } 298.15 \text{ K}) = (57.105 \pm 0.260) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

These entropy values overlap, but result a) was selected for this review, because integration of smoothed  $T$ ,  $C_{p,m}^{\circ}$  data yielded also  $57.18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

### [1978VAS/YAS]

An equation for recalculating thermal effects to zero ionic strength is derived from the Debye-Hückel relation. Numerical values of the coefficients over a wide range of temperatures and ionic strengths are given.

The enthalpy of reaction measured at finite ionic strength can be extrapolated to  $I \rightarrow 0$  by linear regression:  $\Delta_r H - \Delta z^2 \Psi = \Delta_r H^{\circ} + bI$ .

The following table compares the different ionic strength extrapolation functions used in [1967VAS], [1978VAS/YAS] and [1996PLY/GRE]. The agreement between [1967VAS] and [1978VAS/YAS] is not as good as expected.

Table A-39: Molarity to molality conversion.

$I/M$ (HClO <sub>4</sub> )	$I/\text{mol}\cdot\text{kg}^{-1}$ (HClO <sub>4</sub> )	$F(I)$ M basis/ $\text{kJ}\cdot\text{mol}^{-1}$ [1967VAS]	$F(I)$ M basis/ $\text{kJ}\cdot\text{mol}^{-1}$ [1978VAS/YAS]	$F(I)$ m basis/ $\text{kJ}\cdot\text{mol}^{-1}$ [1996PLY/GRE]
0.1000	0.10077	0.1798	0.2096	0.3203
0.5000	0.51330	0.2588	0.3617	0.5144
1.0000	1.05080	0.2874	0.4353	0.6017
2.0000	2.20380	0.3107	0.5085	0.6853
3.0000	3.47130	0.3218	0.5498	0.7313
4.0000	4.86840	0.3286	0.5779	0.7626
6.0000	8.12820	0.3369	0.6154	0.8048

### [1979PAU/STE]

Paukov *et al.* [1979PAU/STE] measured the heat capacity of  $\text{SnCl}_2(\text{cr})$  in the temperature range of 5 to 304.70 K. The values measured for a sample of high purity (99.5%) in a rhombic phase ( $\text{PbCl}_2$ ) are shown in Table A-40 and Table A-41. They estimated the accuracy of the measurements as 0.2% at  $T > 25 \text{ K}$  and about 0.5% at  $T < 25 \text{ K}$ .



Table A-40: Experimental data on heat capacity of SnCl<sub>2</sub>(cr) from [1979PAU/STE].

<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>
5.00	0.3868	28.30	17.97	82.51	52.46	180.16	70.98
5.46	0.5543	29.90	19.28	82.73	52.57	188.08	71.76
5.73	0.6521	33.94	22.66	87.23	54.33	193.56	72.21
6.58	1.018	35.56	23.99	89.35	55.11	200.85	72.89
7.68	1.522	40.08	27.41	95.10	56.69	206.01	73.24
8.68	2.176	41.64	28.72	97.40	57.77	211.62	73.44
9.63	2.768	43.24	29.94	103.32	59.47	218.68	73.84
10.60	3.366	48.20	33.53	105.85	60.10	226.92	74.32
11.54	4.054	49.92	34.88	112.12	61.56	235.08	74.87
12.49	4.752	51.57	36.07	114.91	62.15	243.16	75.28
13.60	5.687	53.14	37.18	121.55	63.58	251.18	75.71
14.67	6.621	57.02	39.70	124.47	64.14	259.45	76.23
15.65	7.376	59.07	40.90	132.29	65.44	267.97	76.67
16.63	8.225	64.27	43.94	138.40	66.27	275.71	77.00
17.55	8.977	66.81	45.38	145.74	67.41	281.67	77.47
18.51	9.749	69.24	46.56	150.70	68.08	289.03	77.67
19.68	10.73	74.66	49.25	155.84	68.66	296.90	77.96
20.86	11.70	77.10	50.14	161.39	69.20	299.12	77.97
21.91	12.59	79.80	51.36	169.08	69.99	303.01	78.23
22.92	13.40	80.61	51.74	174.52	70.52	304.70	78.33

Table A-41: Heat capacity, entropy and enthalpy of SnCl<sub>2</sub>(cr) from [1979PAU/STE].

<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$S_m^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$(H_T - H_{0K})$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$S_m^{\circ}$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$(H_T - H_{0K})$ (SnCl <sub>2</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup>
5	0.4172	0.2206	0.8378	70	46.98	39.09	1602
7	1.226	0.4745	2.390	80	51.47	45.65	2096
9	2.349	0.9139	5.935	90	55.31	51.94	2630
12	4.384	1.859	15.94	100	58.50	57.68	3199
15	6.866	3.101	32.77	150	67.96	83.69	6392
20	10.99	5.640	77.41	200	72.75	104.0	9917
30	19.36	11.67	229.0	250	75.69	120.5	13630
40	27.44	18.36	463.5	273.15	76.94	127.3	15400
50	34.89	25.30	775.7	298.15	78.05	134.1	17330
60	41.49	32.27	1159	300	78.12	134.6	17475

**[1979VAS/GLA]**

Redox potentials for  $\text{Sn}^{4+}/\text{Sn}^{2+}$  in perchloric acid solutions containing  $\text{SnCl}_2$  and  $\text{SnCl}_4$  were determined at 25 °C and ionic strength 2 – 4 M  $\text{HClO}_4$ , using the cell:



After 3 to 3.5 h electrode potentials were stable shifting less than 0.02 mV per hour, thus indicating equilibration. Concentration of  $\text{Sn}^{2+}$  was determined iodometrically after measuring electrode potentials.

Equilibrium concentrations of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  were calculated considering hydrolysis ( $\text{Sn}(\text{OH})^{3+}$ ,  $\text{Sn}(\text{OH})_2^{2+}$ ,  $\text{Sn}(\text{OH})_3^+$ ,  $\text{Sn}(\text{OH})_4$ ) [1971NAZ/ANT] and chlorido complex formation ( $\text{SnCl}^+$ ,  $\text{SnCl}_2$ ,  $\text{SnCl}_3^-$ ) using constants from literature including work of their own group.

The standard potential of the half-cell  $\text{Sn}^{2+}, \text{Sn}^{4+} \mid \text{Hg, Pt}$  according to reaction



was found to be  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.1522 \pm 0.0005)$  V. The calculated Gibbs energy of formation of  $\text{Sn}^{4+}$  in aqueous solution is  $\Delta_f G_m^\circ(\text{Sn}^{4+}) = (1.63 \pm 0.13)$  kJ·mol<sup>-1</sup>.

The results of Vasil'ev *et al.* are flawed by two numerical mistakes.

- (1) While Eqs. (6), (7) and (8) used in [1979VAS/GLA] for extrapolation to ionic strength  $I = 0$  are quite correct,  $-\psi(I)$  has erroneously been ascribed a negative value.
- (2) In the original Table 2 of [1979VAS/GLA] row 13 and 14 of column 8 as well as column 9 should be exchanged.

In addition Vasil'ev *et al.* conclude from earlier experiments [1977VAS/GLA] that  $\text{SnCl}_4$  and  $(\text{NH}_4)_2\text{SnCl}_6$  dissociate completely in 0.6 to 2.0 M  $\text{HClO}_4$ .

In Table A-42 the experimental data of [1979VAS/GLA] are listed. As the SIT method is based on molality as composition variable these data were transformed by the following semi-empirical equation:

$$m_B = c_B \cdot [1/d_w^\circ + a \cdot c_{(\text{ClO}_4^- + \text{Cl}^-)} + b \cdot c_{(\text{ClO}_4^- + \text{Cl}^-)}^2] \quad (\text{A.73})$$

where at 25 °C  $c_B, d_w^\circ = 0.997045$  kg·dm<sup>-3</sup>,  $c_{(\text{ClO}_4^- + \text{Cl}^-)}$ , and  $a = 0.044672$  dm<sup>6</sup>·mol<sup>-1</sup>·kg<sup>-1</sup>,  $b = 0.002291$  dm<sup>9</sup>·mol<sup>-2</sup>·kg<sup>-1</sup> are the concentration of substance B given in Table A-42, the density of pure H<sub>2</sub>O, the total anion concentration, and the empirical fit parameters when Eq. (A.73) is regressed using  $\xi(\text{HClO}_4) = m_{\text{HClO}_4}/c_{\text{HClO}_4}$  listed in Table II-5. In the pertinent case  $c_{\text{HClO}_4} \gg c_{\text{Cl}^-}$  and thus the  $\xi(\text{HClO}_4)$  values should be a reasonable approximation to the real ones.

Table A-42: Concentration basis at 25 °C [1979VAS/GLA].

$c_{\text{HClO}_4} / \text{M}$	$c_{\text{SnCl}_4} / \text{M}$	$c_{\text{SnCl}_2} / \text{M}$	$I / \text{M}$	$[\text{H}^+] / \text{M}$	$[\text{Sn}^{4+}] / \text{M}$	$[\text{Sn}^{2+}] / \text{M}$	$E / \text{V}$
2.000	0.010130	0.023750	2.116	2.011	0.002689	0.012030	0.16340
2.000	0.016330	0.013310	2.140	2.017	0.004352	0.006124	0.17760
2.000	0.019350	0.010600	2.154	2.021	0.005161	0.004784	0.18309
2.000	0.015000	0.018680	2.141	2.016	0.003987	0.008313	0.17190
3.000	0.009208	0.022760	3.111	3.008	0.003423	0.010540	0.15194
3.000	0.005000	0.021840	3.138	3.012	0.005584	0.011470	0.15720
3.000	0.007489	0.026650	3.104	3.006	0.002783	0.013030	0.14650
3.000	0.007598	0.002879	3.110	3.006	0.002824	0.012790	0.14710
3.000	0.017400	0.006085	3.142	3.014	0.006481	0.002603	0.17800
4.000	0.025930	0.004071	4.192	4.019	0.011120	0.001562	0.17880
4.052	0.026510	0.003595	4.221	4.071	0.011470	0.001354	0.17990
4.000	0.026500	0.003500	4.194	4.019	0.011360	0.001347	0.17960
4.000	0.003491	0.023620	4.086	4.030	0.001491	0.011370	0.12771
4.000	0.014720	0.007791	4.117	4.011	0.006289	0.004272	0.15810

The standard potential  $E^\circ$  ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ) of Eq. (A.74) is defined by

$$E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = E - (k/2) \left\{ \log_{10} \left[ \frac{m_{\text{Sn}^{4+}} \cdot p_{\text{H}_2}}{m_{\text{Sn}^{2+}} \cdot m_{\text{H}^+}^2} \right] + \log_{10} \left[ \frac{\gamma_{\text{Sn}^{4+}}}{\gamma_{\text{Sn}^{2+}} \cdot \gamma_{\text{H}^+}^2} \right] \right\}. \quad (\text{A.74})$$

It is assumed that  $\text{H}_2$  is in its standard state, thus  $\log_{10} p_{\text{H}_2} = 0$ .

$$E_m^\circ = E - (k/2) \left\{ \log_{10} \left[ \frac{m_{\text{Sn}^{4+}}}{m_{\text{Sn}^{2+}} \cdot m_{\text{H}^+}^2} \right] \right\} \quad (\text{A.75})$$

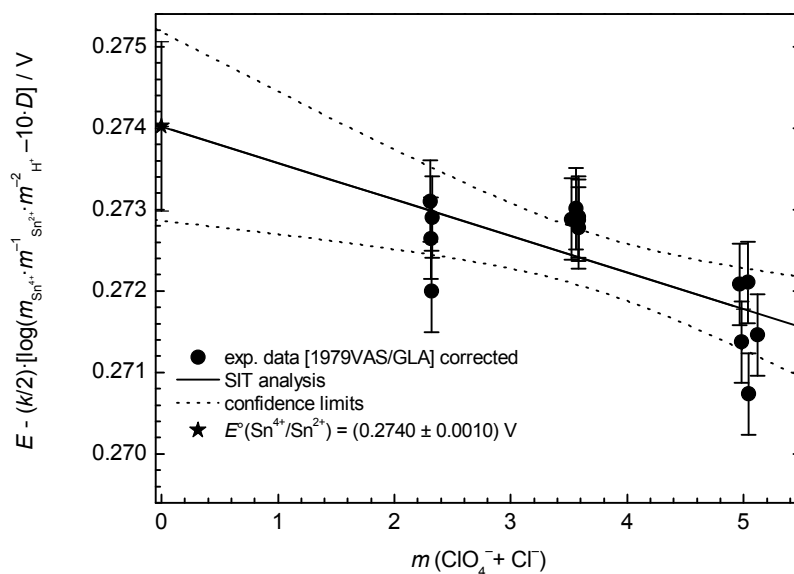
The SIT approach for  $\text{HClO}_4$  as preponderant electrolyte leads to Eqs. (A.76) and (A.77)

$$\log_{10} \left[ \frac{\gamma_{\text{Sn}^{4+}}}{\gamma_{\text{Sn}^{2+}} \cdot \gamma_{\text{H}^+}^2} \right] = \quad (\text{A.76})$$

$$\left\{ -10D + [\varepsilon(\text{Sn}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{Sn}^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-)] \cdot m_{\text{ClO}_4^-} \right\} \\ E_m^\circ + (k/2) \cdot 10D = E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) + \Delta\varepsilon \cdot m_{\text{ClO}_4^-} \quad (\text{A.77})$$

The standard potential  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.2740 \pm 0.0010)$  V arrived at by evaluating these data using the SIT approach, see Figure A-41, agrees reasonably with that recalculated by Hummel *et al.*  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.289 \pm 0.006)$  V [2002HUM/BER], who were the first to recognise the sign error of [1979VAS/GLA].

Figure A-41: SIT analysis of data from [1979VAS/GLA].



This re-evaluation simply attempted to interpret the results presented in [1979VAS/GLA] correctly. In order to perform a SIT analysis the concentrations listed in Table A-42 were converted into molalities, see Table A-43. As shown in Figure A-41 the extrapolation to  $m_{(\text{ClO}_4^- + \text{Cl}^-)} = 0$  clearly resulted in a different value, due to the sign error mentioned above. In contrast to the results of [1978FAT/ROU] and [2009GAJ/SIP] who found highly stable Sn(IV) chlorido complexes Vasil'ev *et al.* disregarded those altogether in their ionic media. Moreover the Sn(IV) hydrolysis constants of [1971NAZ/ANT] are approximate estimates only. Consequently  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.2740 \pm 0.0010)$  V was not used in this review for calculating the finally selected mean value.

Table A-43: Molality basis at 25 °C [1979VAS/GLA].

$c_{(\text{ClO}_4^- + \text{Cl}^-)} /$	$m_{\text{H}^+} /$	$m_{\text{Sn}^{4+}} /$	$m_{\text{Sn}^{2+}} /$	$I /$	$m_{(\text{ClO}_4^- + \text{Cl}^-)} /$	$E /$	$(E_m^0 + k \cdot 5D) /$
M	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	V	V
2.088	2.225	0.002975	0.013308	2.341	2.310	0.16340	0.27310
2.092	2.232	0.004815	0.006776	2.368	2.315	0.17760	0.27265
2.099	2.237	0.005712	0.005295	2.384	2.323	0.18309	0.27291
2.097	2.231	0.004413	0.009200	2.370	2.321	0.17190	0.27200
3.082	3.497	0.003979	0.012252	3.616	3.583	0.15194	0.27287
3.064	3.498	0.006485	0.013320	3.644	3.558	0.15720	0.27301
3.083	3.494	0.003235	0.015147	3.608	3.584	0.14650	0.27277
3.036	3.486	0.003275	0.014833	3.607	3.521	0.14710	0.27288
3.082	3.503	0.007533	0.003026	3.652	3.582	0.17800	0.27291
4.112	4.925	0.013626	0.001914	5.137	5.039	0.17880	0.27211
4.165	5.002	0.014094	0.001664	5.187	5.118	0.17990	0.27146
4.113	4.925	0.013921	0.001651	5.140	5.040	0.17960	0.27074
4.061	4.925	0.001822	0.013896	4.994	4.964	0.12771	0.27208
4.074	4.906	0.007692	0.005225	5.035	4.983	0.15810	0.27138

**[1980AND/SAM]**

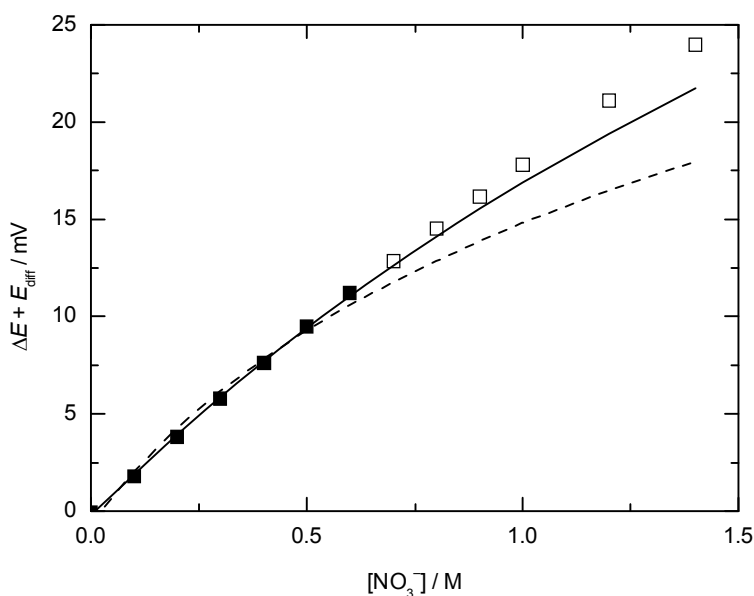
Potentiometric measurements using a capillary tin amalgam electrode have been performed to study the complex formation processes between tin(II) and nitrate ion under nitrogen atmosphere at 25 °C in (Na,H)ClO<sub>4</sub> medium at six different ionic strengths ( $I = 1, 2, 3, 4, 6$  and  $8$  M) by measuring the potential of the following cell:

$\text{Hg} \mid \text{HgCl}_2(\text{s}) \mid 0.1 \text{ M NaCl}, 0.5 \text{ M HClO}_4, I-0.6 \text{ M NaClO}_4 \parallel 0.5 \text{ M HClO}_4, I-0.5 \text{ M NaClO}_4 \parallel I-0.5-x \text{ M NaClO}_4, 0.5 \text{ M HClO}_4, x \text{ M NaNO}_3, 0.001 \text{ M Sn}(\text{ClO}_4)_2 \mid \text{tin amalgam}.$

The diffusion potential of the above cell was estimated in a separate measurement, using NaI instead of Sn(ClO<sub>4</sub>)<sub>2</sub>. Primary experimental data are reported only for  $I = 3$  M. Since the original (Na,H)ClO<sub>4</sub> background electrolyte was almost entirely replaced by NaNO<sub>3</sub> during the measurements, resulting in a substantial change of the activity coefficients, the raw data were re-evaluated for the purposes of this review, using the data points corresponding to  $[\text{NO}_3^-]_{\text{tot}} \leq 0.6$  M (maximum 20% replacement of the background electrolyte). At  $I = 3$  M, the authors reported the formation of three complexes (SnNO<sub>3</sub><sup>+</sup>, Sn(NO<sub>3</sub>)<sub>2</sub>(aq), Sn(NO<sub>3</sub>)<sub>3</sub><sup>-</sup>). Using the above mentioned limited data set, the experimental data can be well reproduced considering the formation of SnNO<sub>3</sub><sup>+</sup>, Sn(NO<sub>3</sub>)<sub>2</sub>(aq) (see Figure A-42). Therefore, the formation of the *tris*-nitrate complex, reported in [1980AND/SAM] is ambiguous, since the differentiation between the complex formation and medium effect is almost impossible

at higher nitrate concentrations. On the other hand, at  $[\text{NO}_3^-] = 0.6 \text{ M}$  only 14% of the total tin(II) is transformed into  $\text{Sn}(\text{NO}_3)_2(\text{aq})$ . Therefore at lower ionic strength, a reasonable value for  $\beta_2$  probably cannot be obtained. For these reasons, in this review only  $\beta_1$  and  $\beta_2$  for  $I \geq 3 \text{ M}$  are considered.

Figure A-42: Experimental cell-potential values reported in [1980AND/SAM] as a function of the nitrate concentration. In the calculations, only the data points for  $[\text{NO}_3^-] \leq 0.6 \text{ M}$  (full squares) were included. Dashed line was calculated by assuming the formation of a single complex ( $\log_{10} \beta_1 = 0.37$ ), the solid line obtained by considering two nitrate complexes ( $\log_{10} \beta_1 = 0.23$ ,  $\log_{10} \beta_2 = 0.04$ ).



#### [1980BER/STE]

Berezovskii *et al.* [1980BER/STE] measured the heat capacity of  $\text{SnBr}_2(\text{cr})$  in the temperature range 5.49 to 32.79 K. In all there were 87 points (see Table A-44).

#### [1980FED/BOL]

The formation of the binary chlorido and thiocyanato as well as the ternary chlorido-thiocyanato complexes of tin(II) was studied by a potentiometric method at ionic strengths of 0.5, 1.0 and 3.0 M  $\text{NaClO}_4$  and 25 °C using a tin amalgam electrode. It seems, that the formation constants of the binary chlorido complexes were taken from [1975FED/BOL]. The authors concluded the formation of three binary thiocyanato

species ( $\text{SnSCN}_q^{2-q}$ ,  $q = 1, 2, 3$ ) and three ternary complexes ( $\text{SnCl}_x\text{SCN}_y^{2-x-y}$ ,  $(x,y) = (1,1), (1,2)$  and  $(2,1)$ ). The Vasil'ev equation has been applied to calculate the thermodynamic formation constants. All measurements were made in ternary tin(II)-chloride-thiocyanate systems, thus separate measurements to determine the formation constants of the binary thiocyanato complexes were not performed. The graphical presentation of the experimental data are provided only for  $I = 1$  M. Based on this information, the  $\text{NaClO}_4$  medium was entirely replaced by  $\text{NaSCN}$  and  $\text{NaCl}$  during the measurements. The re-evaluation of the experimental data is not possible, and an important medium effect can be expected in the region where the *bis*- and *tris*-complexes are formed. Therefore an uncertainty of  $\pm 0.5$  has been assigned to the  $\log_{10} \beta_1$  values of the  $\text{SnSCN}^+$  binary complex, while the formation constants of the species  $\text{Sn}(\text{SCN})_2(\text{aq})$ ,  $\text{SnSCN}_3^-$  and the ternary complexes were not considered any further in this review.

Table A-44: Measured heat capacity data for  $\text{SnBr}_2(\text{cr})$  from [1980BER/STE].

$T/\text{K}$	$C_{p,m}^0$ ( $\text{SnBr}_2, \text{cr}, T$ )/ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0$ ( $\text{SnBr}_2, \text{cr}, T$ )/ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0$ ( $\text{SnBr}_2, \text{cr}, T$ )/ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^0$ ( $\text{SnBr}_2, \text{cr}, T$ )/ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
5.49	0.6077	32.50	29.94	101.40	66.02	207.26	75.48
6.35	0.9315	33.54	31.12	109.12	67.38	212.00	75.67
7.25	1.343	36.73	34.54	112.95	67.90	216.71	75.97
8.22	1.884	37.82	35.65	117.07	68.48	221.37	76.18
10.38	3.419	42.78	40.25	125.25	69.57	235.96	76.71
11.30	4.233	46.47	43.29	129.87	70.13	241.50	76.88
12.24	5.174	47.99	44.49	134.90	70.71	247.00	77.07
13.20	6.249	52.05	47.48	139.83	71.16	252.44	77.28
14.14	7.454	53.98	48.85	144.66	71.57	257.83	77.49
15.08	8.582	55.82	50.00	154.16	72.31	263.19	77.71
16.04	9.674	61.12	53.02	158.82	72.69	268.50	77.92
17.04	10.89	64.24	54.62	163.40	72.98	273.77	78.12
18.14	12.26	67.33	56.24	167.93	73.28	279.69	78.32
19.12	13.49	71.53	57.76	172.40	73.46	286.83	78.70
20.00	14.62	75.02	59.11	176.82	73.86	293.44	78.62
20.92	15.79	82.75	61.61	177.29	73.89	299.03	79.10
21.86	16.97	85.96	62.47	181.72	74.16	304.66	79.22
24.64	20.51	89.05	63.45	186.12	74.41	310.28	79.39
25.65	21.79	92.04	64.04	192.23	74.70	315.86	79.61
28.41	25.15	94.96	64.72	197.37	75.00	321.79	79.89
29.38	26.31	97.95	65.36	202.46	75.26		

**[1980KOS/PAS]**

Koschenko *et al.* [1980KOS/PAS], [1980KOS/DEM] measured the heat capacity of  $\text{Sn}_4\text{As}_3(\text{cr})$  over the temperature range 7 to 315 K. The data are listed in Table A-45 and Table A-46 and the integrated values are shown in Chapter X (Tables X-7 and X-8 respectively for the 58% and the 59% compound).

Table A-45: Experimental values of heat capacity of  $\text{Sn}_4\text{As}_3$  with 58% Sn.

$T/\text{K}$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/\text{K}$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
7.25	1.32	84.00	131.6	229.85	172.9
9.40	3.75	88.15	134.9	233.07	173.0
11.52	7.4	99.99	142.4	235.82	173.5
13.39	11.9	103.5	144.9	239.17	173.6
15.48	16.8	107.61	147.0	241.69	147.0
17.20	20.8	116.89	150.8	244.09	174.3
19.15	25.4	121.27	152.7	247.50	174.7
21.17	29.9	126.39	154.5	250.81	174.8
23.97	36.1	131.40	156.2	253.25	175.1
26.05	40.5	136.28	157.6	255.34	175.1
28.08	46.4	147.90	160.6	258.02	175.2
30.70	50.6	156.81	162.2	261.45	175.6
32.12	53.8	161.28	163.6	264.32	176.2
34.41	56.6	161.80	163.7	267.05	176.5
36.62	63.3	167.25	164.8	270.24	176.9
38.50	67.2	173.14	166.0	273.69	177.2
40.75	71.5	178.95	167.0	276.92	177.5
42.80	75.1	184.69	167.4	280.60	177.8
44.94	79.1	188.07	168.1	283.93	178.1
46.03	80.9	191.96	168.7	287.01	178.4
48.81	85.9	195.41	169.9	290.12	178.9
50.93	89.6	199.20	169.6	291.53	179.1
52.89	92.8	201.04	169.7	291.58	179.4
54.57	95.7	204.25	170.2	294.54	179.6
55.42	99.1	208.09	170.5	296.35	179.5
57.74	102.2	211.36	170.9	297.48	179.6
61.41	107.1	215.44	171.0	300.73	180.0
65.73	112.5	217.77	171.6	303.22	180.2

(Continued on next page)



Table A-45 (continued)

$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
70.29	117.9	221.18	171.7	305.06	180.2
75.13	123.2	223.87	172.2	308.84	180.8
79.67	127.7	227.37	172.4	314.43	181.7

Table A-46: Experimental values of heat capacity of  $\text{Sn}_4\text{As}_3$  with 59% Sn.

$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{Sn}_4\text{As}_3, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
6.72	1.52	70.68	118.7	191.15	169.3
8.21	3.02	74.88	123.3	192.82	169.2
10.59	6.8	78.85	127.8	196.04	169.9
13.20	13.1	83.73	131.5	198.11	170.0
15.45	19.1	86.20	133.6	198.23	170.2
17.53	24.6	88.35	135.3	202.09	170.6
19.16	28.3	89.46	136.1	204.26	170.7
21.94	34.2	91.33	137.4	204.98	170.9
24.03	38.5	94.85	140.0	206.41	171.0
30.58	52.4	106.62	146.7	212.97	171.4
33.90	59.3	110.76	148.5	217.83	172.0
36.05	63.4	118.43	152.1	223.60	172.9
38.70	69.0	122.04	153.6	229.30	173.2
40.79	72.7	128.64	155.3	235.79	174.0
43.81	78.3	131.66	156.3	240.96	174.6
45.24	81.2	134.60	157.6	246.02	175.1
48.19	86.8	137.51	158.3	250.88	175.7
50.28	90.1	140.39	158.9	256.10	176.2
53.62	96.0	143.28	159.5	259.64	176.3
54.20	96.1	146.15	160.2	260.95	176.6
54.93	97.1	148.99	161.4	262.82	176.9
55.43	97.6	152.45	162.1	265.24	177.2
59.12	103.2	160.54	163.7	270.77	177.8
61.00	106.3	165.12	164.3	274.21	178.1
62.34	108.2	170.40	165.5	278.17	178.4
63.36	109.0	175.61	166.4	281.86	178.7
64.34	111.0	181.83	167.5	298.44	180.6
65.53	112.9	186.01	168.2	309.08	181.8
67.37	115.0	189.40	169.0	312.38	181.9

**[1980KOS/PAS2]**

Heat capacity data for SnAs(cr) were measured by Koschenko *et al.* and the data are presented in the following table. The numerically integrated data are presented in Table X-6.

Table A-47: Heat capacity data on SnAs(cr) obtained by [1980KOS/PAS2].

$T/K$	$C_{p,m}^{\circ}(\text{SnAs, cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnAs, cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	$T/K$	$C_{p,m}^{\circ}(\text{SnAs, cr})/$ $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
5.73	0.079	70.82	33.2	176.52	47.6
7.22	0.100	74.07	34.3	181.39	47.8
9.36	0.259	74.24	34.4	186.23	48.0
11.54	0.80	77.30	35.3	191.03	48.2
13.70	2.55	80.50	36.3	195.73	48.4
15.95	2.69	83.59	37.1	201.08	48.6
18.02	3.86	86.52	37.8	205.65	48.7
21.14	5.88	89.38	38.5	210.16	48.9
24.08	7.80	92.59	39.2	215.02	49.0
26.82	9.71	95.31	39.8	220.20	49.2
28.90	11.8	100.84	40.7	225.41	49.4
31.15	12.6	101.53	40.9	230.18	49.5
32.20	13.1	101.70	40.9	235.12	49.7
34.41	14.6	103.58	41.2	243.80	49.9
36.62	15.9	106.35	41.6	248.02	50.0
38.83	17.4	106.28	42.0	252.52	50.1
40.98	18.7	112.38	42.5	257.25	50.2
41.36	19.0	115.41	42.8	261.91	50.3
42.16	19.4	119.14	43.3	266.43	50.5
43.19	20.0	123.55	43.8	271.01	50.6
44.71	20.8	127.86	44.2	276.30	50.7
47.6	22.6	132.23	44.6	281.62	50.8
50.34	24.1	136.26	45.0	286.98	50.9
53.29	25.6	140.24	45.3	292.66	51.0
54.69	26.4	144.17	45.6	296.81	51.1
55.82	27.1	148.06	45.9	297.60	51.2
57.95	28.0	151.91	46.1	299.57	51.3
60.43	29.1	155.72	46.4	300.91	51.3
60.64	29.3	159.69	46.7	304.98	51.3
61.89	29.8	163.62	46.9	309.00	51.4
64.07	30.7	168.43	47.1	310.79	51.5
67.20	31.9	172.21	47.3	312.98	51.6

**[1980ORE/AND]**

In connection with electroplating, the ionic composition and nature of discharging species in a system containing protonated pyrophosphate complexes of tin were studied by polarography at 25 °C in 0.333 M K<sub>2</sub>SO<sub>4</sub> solution under argon atmosphere. The formation of the species Sn(H<sub>x</sub>P<sub>2</sub>O<sub>7</sub>)<sup>x-2</sup> and Sn(H<sub>x</sub>P<sub>2</sub>O<sub>7</sub>)<sub>2</sub><sup>2x-6</sup> was detected with increasing concentration of pyrophosphate ion. The rate constant and the transfer coefficient of the cathodic reaction were studied. Numerical values of the stability constants are not provided.

**[1980ORE/AND2]**

The complex formation between tin(II) and pyrophosphate ion has been studied by potentiometric and spectrophotometric methods at 25 °C and in 0.333 M K<sub>2</sub>SO<sub>4</sub> solution [Sn<sup>2+</sup>]<sub>T</sub> = 1 mM, [P<sub>2</sub>O<sub>7</sub><sup>4-</sup>]<sub>T</sub> = 5 to 100 mM. Nine different pyrophosphato complexes were identified (SnH<sub>x</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>y</sub><sup>2+x-4y</sup>, with (x,y) = (0,1), (1,1), (2,1), (0,2), (1,2), (2,2), (3,2), (4,2)) and the equilibrium constants of their formation reactions were calculated (in case of SnH<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub><sup>4-</sup> two protonation isomers were reported). The data were used to develop a bath for Sn electroplating. The protonation constants of pyrophosphate are not given in the paper and were taken from an untraceable book (Yu. F. Zdanov, Chemistry and technology of polyphosphates, Khimiya, 1979). Due to the relatively strong association between alkali metal ions and the differently protonated pyrophosphates, the protonation of pyrophosphate and the tin(II)-pyrophosphate systems should be investigated under strictly identical conditions, and the potassium complexes of pyrophosphate have to be taken into account at [K<sup>+</sup>]<sub>T</sub> > 0.1 – 0.2 M. This is not the case in [1980ORE/AND2]. Furthermore, the potassium sulfate is not an inert background electrolyte, since the sulfate ion forms complexes with tin(II). Therefore the constants reported in [1980ORE/AND2] are not considered any further in this review.

**[1980PAN/DEN]**

The blue-black modification of SnO is isostructural with the tetragonal form of PbO but is the only example of a regular square-pyramidal tin(II) coordination. A neutron study was undertaken to check this tin(II) configuration which finally was confirmed indeed.

SnO, tetragonal, *P4/nmm*,  $a_0/\text{Å} = 3.8029(5)$ ,  $c_0/\text{Å} = 4.8328(8)$  (neutrons, 293 K),  $Z = 2$ . Profile and integrated-intensity refinements at room temperature confirm the regular square-pyramidal coordination of Sn(II), with Sn–O 2.224(8) Å. Final *R* for the integrated-intensity refinement was 4.3% for 28 measured intensities. The thermal expansion is less anisotropic than expected for a layer structure.

From the above unit cell parameters the density of SnO(tetr) is calculated to be  $\rho = (6393.9 \pm 2.7) \text{ kg}\cdot\text{m}^{-3}$ .

**[1980SMO/YAK]**

Smolyarenko and Yakimovich [1980SMO/YAK] investigated the potential difference of the galvanic cell



between 655 and 766 K to determine the thermodynamic data of the compound  $\text{ZnSnAs}_2(\text{s})$ . This is not a stoichiometric compound but the spread in the compositional range is quite narrow and therefore, the measured data are meaningful. The variations in thermodynamic properties are so small that they can be ignored.

The following equation of the temperature dependence of the cell potential was obtained:

$$E/\text{mV} = 109.74 - 0.0902 (T/\text{K}) \pm 2 [1.08/36 + 0.24 \times 10^{-4} ((T/\text{K}) - 711.8)^{1/2}].$$

For the potential-forming reaction of the cell  $\text{Sn(l)} + \text{ZnAs}_2(\text{s}) \rightleftharpoons \text{ZnSnAs}_2(\text{s})$ , the thermodynamic data within the temperature range investigated (655 to 766 K) are:

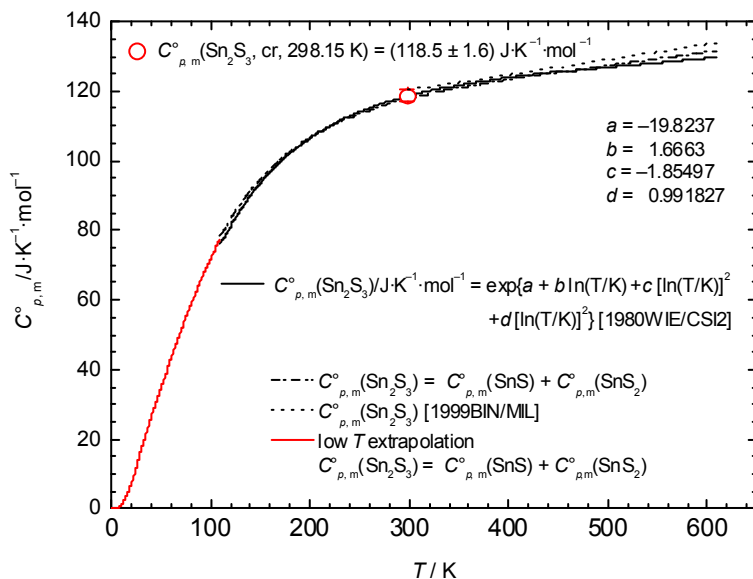
$$\Delta_r H_m^\circ = -(21.174 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}, \quad \Delta_r S_m^\circ = (17.405 \pm 1.7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ and } \Delta_r G_m^\circ = (21.17 - 0.174 T) \text{ kJ}\cdot\text{mol}^{-1}.$$

The calculated standard thermodynamic functions of formation of  $\text{ZnSnAs}_2(\text{s})$  from solid Sn, Zn, and As are:  $\Delta_f G_m^\circ(\text{ZnSnAs}_2, \text{s}, 298.15 \text{ K}) = -(77.4 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{ZnSnAs}_2, \text{s}, 298.15 \text{ K}) = -(87.03 \pm 3.00) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $S_m^\circ(\text{ZnSnAs}_2, \text{s}, 298.15 \text{ K}) = -(31.8 \pm 3.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

These data cannot be accepted because of the estimated data used in the calculations.

**[1980WIE/CSI]**

The heat capacity of  $\text{Sn}_2\text{S}_3$  was measured in the temperature range 110–610 K, employing a differential scanning calorimeter. The sum of the heat capacities of SnS and  $\text{SnS}_2$  [1953KIN/TOD], [1958ORR/CHR] agreed with the measured heat capacity of  $\text{Sn}_2\text{S}_3$  from 110 to 610 K, see Figure A-43. Structural and bonding similarities between  $\text{Sn}_2\text{S}_3$ , SnS and  $\text{SnS}_2$  justify the extrapolation of the heat capacity of  $\text{Sn}_2\text{S}_3$  from 110 to 0 K, using the sum of the heat capacities, SnS and  $\text{SnS}_2$ . With the measured and extrapolated heat capacity data of  $\text{Sn}_2\text{S}_3$ , the entropy, enthalpy increment and Gibbs energy function have been evaluated.  $S^\circ(298.15 \text{ K}) = (163.6 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = (23.7 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  and  $G^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = -(25.1 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{Sn}_2\text{S}_3$ .

Figure A-43: Heat-capacity function of  $\text{Sn}_2\text{S}_3(\text{cr})$ .

Wiedemeier *et al.*'s fitting functions summarised below are very useful for calculating thermodynamic parameters of tin sulfides, see, for example, Figure A-44.

$$[C_{p,m}^{\circ}]_{100\text{K}}^{875\text{K}}(\text{SnS}, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.3})$$

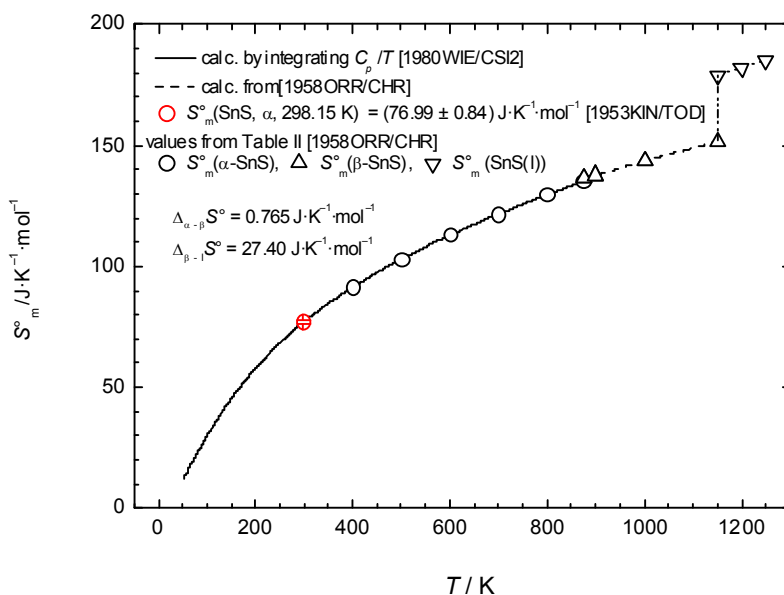
where  $a = -19.1440$ ,  $b = 11.6659$ ,  $c = -1.99273$  and  $d = 0.114905$  [1980WIE/CSI2].

$$[C_{p,m}^{\circ}]_{110\text{K}}^{610\text{K}}(\text{Sn}_2\text{S}_3, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.4})$$

where  $a = -19.8237$ ,  $b = 11.6663$ ,  $c = -1.85497$  and  $d = 0.0991872$  [1980WIE/CSI2].

$$[C_{p,m}^{\circ}]_{100\text{K}}^{1005\text{K}}(\text{SnS}_2, \alpha, T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = \exp\{a + b \ln(T/\text{K}) + c [\ln(T/\text{K})]^2 + d [\ln(T/\text{K})]^3\} \quad (\text{IX.5})$$

where  $a = -23.6488$ ,  $b = 13.2230$ ,  $c = -2.10132$  and  $d = 0.112224$  [1980WIE/CSI2].

Figure A-44: Entropy function of  $\text{Sn}_2\text{S}_3(\text{cr})$ .**[1980ZHO/KOS]**

The specific heat of crystalline tin dioxide has been measured in an adiabatic calorimeter with periodic heat input, and the thermodynamic functions  $(H_T - H_0)/T$ ,  $S_T - S_0$ , and  $-(G_T - H_0)/T$  have been calculated from the results. Some discrepancies with [1929MIL2] are noted, and ascribed to the method of sample preparation.

Heat capacity data for tetragonal tin dioxide have been measured by the authors. They are presented in Table A-48.

**[1981BAC/HSU]**

Fig. 2 of this paper shows a plot of the characteristic temperature  $\theta_D$  ( $\text{SnO}_2$ ) versus  $T$  in the range  $0 \leq T \leq 20 \text{ K}$ . From this data the Debye temperature was estimated to be  $\theta_D(\text{SnO}_2) = (500 \pm 30) \text{ K}$ .

Table A-48: Heat capacity data on tetragonal tin dioxide.

$T/K$	$C_{p,m}^o(\text{SnO}_2, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^o(\text{SnO}_2, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$T/K$	$C_{p,m}^o(\text{SnO}_2, \text{cr})/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
9.7000	0.0335	82.9400	14.5603	188.2700	38.3003
10.3400	$4.1840 \times 10^{-3}$	85.9600	15.6272	192.9500	39.3212
13.4900	0.0711	91.0300	16.9870	200.5400	40.6392
15.2300	0.0669	96.4200	18.3050	205.3700	41.3212
17.7200	0.1548	101.8200	19.6230	210.3800	42.0492
19.2700	0.2552	108.2200	21.3175	215.3500	42.8023
21.1700	0.3640	113.3500	22.6271	220.2300	43.5554
23.4200	4.7321	118.6400	23.8990	225.1000	44.2667
28.2000	1.0795	123.7900	25.0036	230.1800	45.0198
29.5600	1.3305	128.9500	26.1877	235.1700	45.6056
31.8300	1.7447	135.2400	27.5433	239.5800	46.3169
34.3400	2.2092	138.7000	28.5432	246.1200	47.1955
37.8700	2.8200	149.3600	30.7231	252.5300	48.1578
42.4500	3.9539	153.8100	31.4009	257.3200	48.6181
50.1600	5.3639	158.6400	32.3549	265.8600	49.7478
54.9000	6.8994	163.7000	33.5431	274.7300	50.6682
60.0100	7.8450	171.1700	34.9490	283.4900	51.5469
75.0800	12.5478	174.5000	35.5389	289.9300	52.3000
78.6400	13.3470	179.9000	36.6058	295.3500	52.9694
				301.3100	53.5134

**[1981CHE]**

Mössbauer spectroscopy was the first time applied to the determination of complex formation constants. The Mössbauer spectra of the frozen aqueous solutions containing tin(IV) and fluoride ion showed the averaged state of the equilibrium species, and their isomer shift values could be expressed as a linear function of the mole fraction of the consecutively formed complex species. The author claimed that  $\log_{10} \beta_N$  ( $N$  = maximal coordination number) can be obtained simply from the ligand concentration at the half-value point of the Mössbauer isomer shift – ligand concentration curve. The method was applied to  $\text{SnF}_6^{2-}$  complex, and  $\log_{10} \beta_6 = 24.5$  has been determined. Although, this value is close to that determined in [1954SCH/DAV] ( $\log_{10} \beta_6 = 25$ ), this is a greatly simplified method for the determination of complex formation constants. Moreover, since the complexing ligand is added to the rather concentrated tin(IV) solution (0.22 M) without the use of background electrolyte, the ionic strength continuously changed during the measurements. Therefore, the obtained value can be regarded only

as a very rough approximation. Further complication is raised from the fact that frozen solutions have to be used in Mössbauer spectroscopy. The time needed to cool the samples to liquid nitrogen temperature is 1 to 10 s. Therefore the temperature at which the equilibrium 'was frozen' is unknown.

### [1981CHE2]

Mössbauer spectroscopy was used to determine the formation constants of  $\text{SnCl}_x^{4-x}$  complexes in 0 to 12 M HCl solutions (background electrolyte was not used). The reported isomer shift, the average value of the species present in the solution, showed continuous change up to 12 M HCl, which would indicate rather low stability of the tin(IV)-chlorido complexes. From their data the authors calculated  $\log_{10} \beta_1 = 1.3$ ,  $\log_{10} \beta_2 = 2.1$ ,  $\log_{10} \beta_3 = 2.3$ ,  $\log_{10} \beta_4 = 2.1$ ,  $\log_{10} \beta_5 = 1.4$ ,  $\log_{10} \beta_6^0 = 0.4$ , and by activity correction  $\log_{10} \beta_6^0 = 1.6$ . These data suggest surprisingly weak complex formation for tin(IV), similar to tin(II). The reason of the 8 to 10 orders of magnitude difference from the other reports ([1978FAT/ROU], [2009GAJ/SIP]) is unknown, but as mentioned in the Appendix A entry of [1981CHE], the used method provide only a very rough approximation of complex formation constants.

### [1981CHE/HSU]

Mössbauer spectroscopy was used to determine the formation constants of  $\text{SnF}_x^{2-x}$  ( $x = 1, 2, 3$ ) complexes by adding aqueous HF to a solution containing 0.53 M  $\text{Sn}(\text{ClO}_4)_2$  and 0.59 M  $\text{HClO}_4$  (the ionic strength was not kept constant). Both the observed isomer shift and quadrupole splitting showed characteristic changes by complex formation. The formation constants determined by the authors (see Table VIII.7) are relatively close to the other values in the table, nevertheless these constants were not used to derive selected data (see also the Appendix A entry of [1981CHE]).

### [1981FAT/CHE]

The redox reaction of the Sn(II)/Sn(IV) system was studied in aqueous HCl solutions by steady-state and transient methods under potentiostatic conditions. It was shown that the rate of the electrochemical reaction is inhibited with increasing reactant concentration. This behaviour was quantitatively interpreted using a model in which a homogeneous chemical reaction between the product and the reactant is coupled to charge transfer at the electrode. The kinetic parameters were calculated. from this model by using a computer simulation technique. Excellent agreement with all the experimental results was obtained.

This paper deals essentially with kinetics and mechanism of the redox reaction in the Sn(II)/Sn(IV) system, but it contains a cursory information on the standard electrode potential of  $\text{Sn}^{4+}/\text{Sn}^{2+}$ . The authors claim to have determined  $E_{\text{app}}^0$  ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ) in 6 M HCl with a mercury indicator electrode and presumably the saturated calomel reference electrode. The value obtained was  $-145.4$  mV which leads to



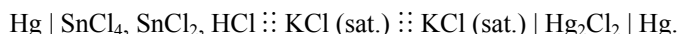
$$E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}, 6.0 \text{ M HCl}, 298.15 \text{ K}) = 99.0 \text{ mV}$$

vs. the standard hydrogen electrode (SHE), as  $E_{\text{h}}^{\circ}(\text{SCE}) = 244.4 \text{ mV}$  [1961IVE/JAN]. The authors state in this context that  $130 \text{ mV (NHE)} = -138 \text{ mV (SCE)}$ , which would be correct for the standard calomel electrode, leading to

$$E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}, 6.0 \text{ M HCl}, 298.15 \text{ K}) = 122.6 \text{ mV}.$$

Unfortunately the authors fail to clearly identify their reference electrode, consequently it cannot be decided which value is the correct one.

Probably the following cell was used



Regardless of the meagre experimental details the advantage of these measurements is that in  $6 \text{ M} = 6.8508 \text{ mol}\cdot\text{kg}^{-1}$  HCl Sn(IV) hydrolysis can no longer play an important role. Thus provided a series of such cell-potential data in, say, 4, 5, 6, 7 molal HCl would exist  $E^{\circ}(\text{Sn}^{4+}/\text{Sn}^{2+}, 298.15 \text{ K})$  could probably be derived without taking Sn(IV) hydrolysis into consideration.

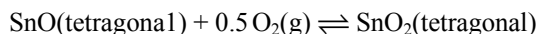
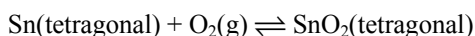
#### [1981IZU]

The Rietveld profile-analysis refinement procedure has been applied to X-ray powder diffractometer data collected from tin(II) oxide with  $\text{CuK}\alpha$  radiation. Four symmetric profile functions were tested; the use of a modified or an intermediate Lorentz function led to a more satisfactory fit than the use of the Gauss or Lorentz function. The positional parameter of the tin atom was found to be 0.2369, which is almost identical with the corresponding value reported for isomorphous lead(II) oxide.

With the unit cell parameters,  $a_0/\text{\AA} = 3.7986(1)$ ,  $c_0/\text{\AA} = 4.8408(2)$ ,  $Z = 2$ , the density of SnO(tetr.) is calculated to be  $\rho = (6409 \pm 1) \text{ kg}\cdot\text{m}^{-3}$ .

#### [1981LAV/TIM]

Lavut *et al.* used combustion calorimetry to measure the enthalpy of reaction of tin (IV) and tin (II) oxides yielding the energies of the reactions:



and the enthalpies of formation of  $\text{SnO}_2(\text{cr})$ , and  $\text{SnO}(\text{cr})$  were calculated.

They emphasise that particular attention was given to the analytical characteristics of the starting samples. They employed two different samples and characterised the sample to a purity of 99.99% or better. They also used X-ray diffraction and showed the crystals to belong to the tetragonal system. They carefully timed the experiments to attain equilibrium for two hours prior to commencement of the measurement. The duration of the main period was 1 hour. Relevant checks showed that

the observance of these conditions made it possible to obtain an error of 0.005 per cent maximum associated with the conditions in the initial and the final periods of the calorimetric experiment in the ultimate result. They made critical calorimeter calibration by running several experiments.

Lavut *et al.* also ensured the reliability of determining the completeness of the reaction occurring in the combustion bomb. The degree of combustion completeness in the first experiment equaled 99.94%. In other experiments, precautions were taken to avoid an incomplete combustion of the sample resulting in the degree of tin (II) oxide combustion between 99.98 to 100.0%.

The value of the standard enthalpy of formation of tin(II) oxide  $\Delta_f H_m^\circ$  (SnO, cr, 298.15 K) =  $-(280.71 \pm 0.21)$  kJ·mol<sup>-1</sup> differs from that reported in Humphrey and O'Brien [1953HUM/OBR], *i.e.*  $-(285.98 \pm 0.67)$  kJ·mol<sup>-1</sup> by almost 2%. The authors ascribe the discrepancy to a) a possible tin(II) oxide evaporation in analyses that require heating of tin (II) oxide; b) the increase in the measured energy of combustion of tin(II) in oxide by 0.692%<sup>1</sup> as against 0.502% required for 99.5% content of tin(II) oxide in the sample; c) the reported results of tin(II) oxide analysis characterised by an imbalance of 0.07%. Finally although the tin(II) oxide combustion did not involve any water introduction into the bomb, a part of the water which evaporated from the sample remained in the gaseous state.

The authors considered the possible hydration of their samples and argued that this could not affect their measurements significantly.

### [1981PET/MIL]

The formation of hydroxido, chlorido, bromido and sulfato complexes of tin(II) was studied at 20 °C by differential pulse anodic stripping voltammetry, using very low ( $5.4 \times 10^{-7}$  M) tin(II) concentration. The authors measured the peak potential in various ionic media (NaNO<sub>3</sub>, NaClO<sub>4</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaBr, HNO<sub>3</sub>, HClO<sub>4</sub> and artificial seawater) at different ionic strengths and at pH = 2 (and between pH 4 and 11 for studying the hydroxido complexes). With the exception of NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaBr and artificial seawater, the peak potential was found to be constant ( $E_{app,free} = (0.442 \pm 0.001)$  V vs. SCE). This indicates that the formation of nitrate complexes cannot be detected under the conditions used. On the other hand, nitrate complexes with measurable stability were reported in [1980AND/SAM] using rather different experimental conditions and methods.

The graphically presented experimental data in [1981PET/MIL] were digitalised and re-evaluated for the purposes of this review. The formation of nitrate complexes was neglected during the re-evaluation, but the uncertainties of the resulting

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<sup>1</sup> The statement is incorrect because this error includes other corrections including water and CO<sub>2</sub> contamination.

constants were increased, due to their possible presence. Since very low tin(II) concentration was used, only mononuclear  $\text{Sn}(\text{OH})^+$ ,  $\text{Sn}(\text{OH})_2(\text{aq})$  and  $\text{Sn}(\text{OH})_3^-$  complexes were detected. The experimental data were linearised and the authors calculated the hydrolysis constants using a stepwise manner (first  $\log_{10} \beta_{1,1}^*$  and  $\log_{10} \beta_{2,1}^*$  then  $\log_{10} \beta_{2,1}^*$  and  $\log_{10} \beta_{3,1}^*$  were calculated).

Except for a few cases, the re-evaluated and originally reported constants agree within  $\pm 0.2$  log units (see Table VII-1). In 0.5 M NaCl solution the authors reported the formation of both  $\text{Sn}(\text{OH})^+$  and  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$ . By comparing the values of  $\log_{10} \beta_{1,1}^*$  obtained in NaCl and  $\text{NaNO}_3$  media, the authors estimated the formation constants of  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$  in 0.5 M NaCl solution ( $\beta_{1,1,\text{Cl}}^* = -(2.9 \pm 0.2)$ ).

The chlorido, bromido and sulfato complexes were studied either at constant ionic strength or in self-medium using increasing concentrations of NaCl, NaBr or  $\text{Na}_2\text{SO}_4$ . The experiments performed in self-medium were re-evaluated for the purposes of this review, using the SIT. The limited number of data did not allow the parallel refinement of all the parameters ( $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ,  $\Delta\alpha(1)$ ,  $\Delta\alpha(2)$ ,  $\Delta\alpha(3)$ ) required for a correct SIT treatment. A 'manually controlled' fitting, refinement of only two parameters in the same time, revealed the formation of complexes  $\text{SnX}_q$  ( $q = 1$  to 3 for  $\text{X} = \text{Cl}^-$  and  $\text{Br}^-$ , while  $q = 1, 2$  for  $\text{X} = \text{SO}_4^{2-}$ ). The following parameters were obtained:  $\log_{10} \beta_1^{\circ} = 1.25$  ( $\Delta\alpha(\text{NaCl}) = 0.08 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_2^{\circ} = 1.99$  ( $\Delta\alpha(\text{NaCl}) = 0.0 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_3^{\circ} = 1.94$  ( $\Delta\alpha(\text{NaCl}) = -0.29 \text{ kg}\cdot\text{mol}^{-1}$ );  $\log_{10} \beta_1^{\circ} = 0.95$  ( $\Delta\alpha(\text{NaBr}) = -0.06 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_2^{\circ} = 2.01$  ( $\Delta\alpha(\text{NaBr}) = -0.09 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_3^{\circ} = 2.31$  ( $\Delta\alpha(\text{NaBr}) = -0.17 \text{ kg}\cdot\text{mol}^{-1}$ );  $\log_{10} \beta_1^{\circ} = 2.2$  ( $\Delta\alpha(\text{Na}_2\text{SO}_4) = -0.17 \text{ kg}\cdot\text{mol}^{-1}$ ),  $\log_{10} \beta_2^{\circ} = 2.7$  ( $\Delta\alpha(\text{Na}_2\text{SO}_4) = -0.11 \text{ kg}\cdot\text{mol}^{-1}$ ). In the case of sulphate, the calculated constants were largely dependent on the choice of eliminated 1-2 outlying points. Considering the mentioned difficulties in the refinement, an uncertainty of  $\pm 0.5$  has been assigned to the above  $\log_{10} \beta_q^{\circ}$  values.

At constant ionic strength (1.0 M  $\text{Na}(\text{NO}_3, \text{X})$  or 1.5 M  $\text{Na}(\text{NO}_3, \text{SO}_4)$ ) the background electrolytes were almost completely replaced by the sodium salt of the complex forming anion. These experiments were also re-evaluated, although due to the continuous change of background electrolyte the resulting formation constants are questionable.

### [1981SCH/NES]

$\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  has been shown to be the correct composition of the so-called basic tin(II) chloride. Well crystallised colourless platelets of pearly luster were precipitated from homogeneous solution. The structure ( $R32-D^3_7$ ,  $a = 1001.8 \text{ pm}$ ,  $c = 4403.0 \text{ pm}$ ,  $Z = 3$ ,  $R = 0.045$ ) was determined from single crystal X-ray diffraction data, corrected for absorption and twinning.

The compound  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  is structurally identical with crystals investigated by [1963DON/MOS], although the composition of the latter was found to be  $\text{Sn}_4\text{Cl}_2(\text{OH})_6$ . Von Schnering *et al.* could not explain this fact.

### [1982MAC]

This paper describes the composition of and the minerals identified in ‘copper’ concretions found on shipwrecks off the Western Australian Coast. Since the copper, brass and bronze artefacts examined have been in a marine environment for periods of up to 350 years they provide valuable information on the long-term stability of these metals to corrosion. Concretions formed on bronzes have tin present in the concretions mainly as the tin(IV) oxide,  $\text{SnO}_2$ , cassiterite with tin(II) oxide sulfate ( $\text{Sn}_3\text{O}_2\text{SO}_4$ ) as a minor phase.

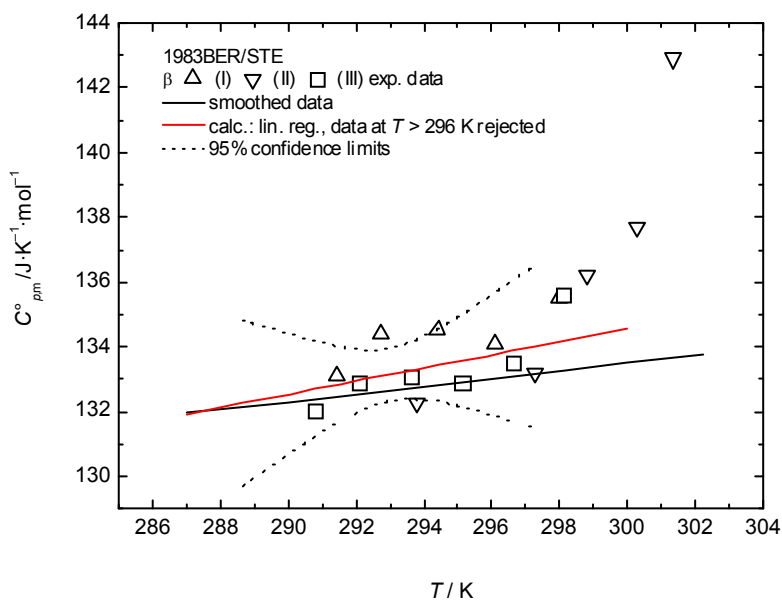
### [1983BER/STE]

Berezovskii *et al.* [1983BER/STE] measured the heat capacity of tin tetrabromide at 112 points in the temperature range 6.66 to 336.2 K in a vacuum adiabatic calorimeter with a nickel bulb [1978BER/PAU], and calculated entropy, enthalpy and Planck function of tin tetrabromide phases  $\alpha$ - $\text{SnBr}_4$ , (monoclinic to 287 K),  $\beta$ - $\text{SnBr}_4$  and  $\text{SnBr}_4$ (liquid) The average deviation of the experimental heat capacities from the smoothed curve was 0.2% below 20 K, 0.05% in the range 20 to 285 K, and 0.1% for the liquid phase (306 to 336 K). For the  $\beta$ -phase (the region of existence of  $\beta$ - $\text{SnBr}_4$ , is 287 to 302 K), three series of experimental points were obtained in the range from 290.9 to 301.9 K (see Table A-49) with relative errors up to 1%. The  $C_p$  data for the  $\beta$ -phase showed above 296 K a “prefusional” increase and the smoothed values selected by the authors are somewhat ambiguous, see Figure A-45. The influence of this discrepancy on the calculated thermodynamic quantities  $S_m^\circ$  ( $\text{SnBr}_4$ ,  $\beta$ , 298.15 K),  $H^\circ(T) - H^\circ(0)$  and  $\Phi^\circ(T)$  is negligible when all other experimental errors are taken into account. In addition to  $C_p$  data listed in Table A-49 Bereszovskii *et al.* determined thermodynamic quantities for the polymorphic phase transition and fusion of  $\text{SnBr}_4$ , see Table A-50.

Table A-49: Heat capacity measurements form SnBr<sub>4</sub>(cr) from [1983BER/STE].

<i>T</i> /K	$C_{p,m}^{\circ}$ (SnBr <sub>4</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnBr <sub>4</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnBr <sub>4</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnBr <sub>4</sub> , cr, <i>T</i> )/ J·mol <sup>-1</sup> ·K <sup>-1</sup>
	α-phase	38.98	64.63	172.99	117.6		β-phase
		40.92	66.64	176.52	118.1		Series I
6.66	3.325	45.40	70.80	180.55	118.8	291.40	133.1
7.05	3.975	47.28	72.36	185.08	119.5	293.73	134.4
7.58	4.742	51.86	75.95	190.07	120.03	294.40	134.5
7.95	5.593	54.24	77.66	195.17	121.0	296.06	134.1
8.60	6.493	56.70	79.30	200.21	121.7	297.98	136.5
8.34	6.948	59.74	81.16	205.21	122.4		Series II
9.70	8.616	63.10	83.13	210.19	123.0	295.78	132.3
9.72	8.691	66.85	85.21	215.21	123.6	297.29	133.2
10.68	10.78	70.67	87.17	220.18	124.2	298.76	136.2
11.64	13.10	74.28	89.00	225.10	124.8	300.26	137.7
12.62	15.61	77.96	90.76	230.91	125.5	301.36	142.0
13.62	18.40	81.22	92.47	235.28	126.0	301.90	227.4*
14.68	21.45	84.14	93.62	240.28	126.5		Series III
15.73	24.012	86.33	94.55	245.57	127.1	290.79	132.0
16.91	26.80	91.06	97.80	250.48	127.7	292.09	132.9
17.94	29.21	99.35	99.80	251.83	127.8	293.61	133.1
18.89	31.36	104.88	101.6	251.56	128.2	296.12	132.9
19.87	33.67	109.76	103.3	259.01	128.6	296.63	133.5
21.02	36.21	114.22	104.4	263.58	129.3	298.11	135.6
22.34	39.01	119.24	105.9	268.11	129.7		Liquid phase
25.52	45.22	128.30	108.6	272.62	130.2		
26.86	47.71	131.63	109.2	275.53	130.1	306.93	163.4
28.27	50.08	140.69	111.3	283.45	131.0	311.32	163.3
28.74	50.87	150.09	113.3	285.72	130.9	314.92	162.9
29.89	52.80	154.36	114.1			319.87	162.6
30.39	53.50	158.94	115.1			325.20	162.3
33.53	58.03	163.44	116.0			330.50	162.0
35.23	60.28	168.25	116.9			336.18	161.8

\* This point is an outlier and was not taken into account for the fitting of the heat capacity data.

Figure A-45: Heat capacity data for  $\beta$ -SnBr<sub>4</sub>.Table A-50: Thermodynamic quantities for phase transitions of SnBr<sub>4</sub>(cr).

Transition	$\alpha \rightarrow \beta$	$\beta \rightarrow \text{liquid}$
$T/\text{K}$	$287.0 \pm 0.1$	$302.25 \pm 0.05$
$\Delta_{\text{us}}H_{\text{m}}^{\circ} / \text{J}\cdot\text{mol}^{-1}$	$1083 \pm 3$	$1250 \pm 30$
$\Delta_{\text{us}}S_{\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$3.774 \pm 0.010$	$40.20 \pm 0.10$

**[1983TOP/KOC]**

Precipitation and dissolution of SnS<sub>2</sub> was investigated in aqueous solutions of HCl and CaCl<sub>2</sub> at 25 °C and 1 atm H<sub>2</sub>S. SnCl<sub>4</sub> is used as starting material. Approaching the equilibrium by precipitation and dissolution shows that at high chloride concentration (5 M) equilibration times of 2 to 3 months are required. Solid phases were identified by X-ray analysis. Concentration of tin was determined by complexometric titration and chloride content also volumetrically by the method of Volhard. No polymorphic phase alterations were observed during ripening of the solid in solution. Precipitation of SnS<sub>2</sub> is accompanied by formation of orthorhombic sulfur. The following table of solubility data is given.

Table A-51: Solubility of SnS<sub>2</sub> in HCl.

[HCl]/M	[Sn] × 100/M	[HCl]/M	[Sn] × 100/M
3.60	0.0042	4.66	8.76
4.00	0.13	4.73	11.88
4.28	5.32	4.74	21.49

Equilibrium data are listed in Table A-52.

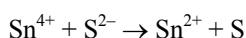
Table A-52: Solubility of SnS<sub>2</sub> in CaCl<sub>2</sub>-HCl solutions.

[HCl]/M	[CaCl <sub>2</sub> ]/M	[Sn] × 100/M	[HCl]/M	[CaCl <sub>2</sub> ]/M	[Sn] × 100/M
1.0	1.35	0.27	4.0	2.25	13.69
4.0	1.35	8.70	1.0	2.25	1.59
1.0	3.15	2.49	2.5	3.15	6.88
4.0	3.15	18.96	2.5	1.35	3.20
			2.5	2.25	4.52

From the results of Table A-52 an equation for the equilibrium tin concentration was derived (for the sake of brevity division by M was omitted):

$$[\text{Sn}] = 1/100 \times (4.33 - 6.33 [\text{HCl}] - 0.85 [\text{CaCl}_2] + 1.78 [\text{HCl}] \times [\text{CaCl}_2] + 1.45 [\text{HCl}]^2).$$

It is not clear to which extent the solubility data are influenced by the formation of sulfur, because of the redox reaction



a certain amount of Sn(II) is formed, precipitated as SnS or not. In any case the solubility data of this paper should represent an upper limit. Chlorido-complex formation plays an important role. No comment on hydrolysis of SnCl<sub>4</sub> is given.

### [1984CHE/HSU]

Mössbauer spectroscopy was used to determine the formation constants of SnCl<sub>x</sub><sup>2-x</sup> (x = 1, 2, 3) complexes by adding aqueous NaCl (0 to 3 M) to a solution containing 0.05 M Sn(ClO<sub>4</sub>)<sub>2</sub> and 0.5 M HClO<sub>4</sub> (I = 3.5 M (Na,H)(ClO<sub>4</sub>/Cl)). This is a more accurate study than the authors' previous reports ([1981CHE], [1981CHE2]), nevertheless this paper also suffers some deficiency: (i) during the measurements the 3 M NaClO<sub>4</sub> background electrolyte was entirely replaced by NaCl, (ii) since fast frozen solutions were used, the temperature at which the equilibrium 'was frozen' is unknown. Although the formation constants determined by the authors based on the shift of quadrupole splitting (see Table VIII-8) are relatively close to the other values in the table, these constants were not used to derive selected data. The authors also studied the

possible complex formation between tin(II) and perchlorate ion, and concluded that no complex formation occurs in the studied concentration range (0.05 M  $\text{Sn}(\text{ClO}_4)_2$ , 0.5 M  $\text{HClO}_4$  and 0 to 4.0 M  $\text{NaClO}_4$ ).

#### [1984HSU/CHE]

Mössbauer spectroscopy was used to determine the formation constants of  $\text{SnBr}_x^{2-x}$  ( $x = 1, 2, 3$ ) complexes by adding aqueous  $\text{NaBr}$  (0 to 1 M) to a solution containing 0.05 M  $\text{Sn}(\text{ClO}_4)_2$  and 0.5 M  $\text{HClO}_4$  ( $I = 3.5$  M (Na,H)( $\text{ClO}_4/\text{Br}$ )). Due to the relatively low excess of bromide used, at the end of the titration the complexation reached only  $\bar{n} = 1.7$  ( $\bar{n}$  = averaged ligand number),  $\log_{10} K_3$  cannot be determined with acceptable accuracy. As fast frozen solutions have to be used in Mössbauer spectroscopy, the temperature at which the equilibrium 'was frozen' is also unknown. Therefore, though the formation constants determined by the authors based on the shift of quadrupole splitting (see Table VIII-11) are relatively close to the other values in the table, these constants were not used to derive selected data.

#### [1984ICH/TAK]

The precipitates obtained by addition of a solution of  $\text{NaHCO}_3$  to a solution of  $\text{SnCl}_2$  at various pH were studied by thermal analysis, Mössbauer spectroscopy, and X-ray powder diffraction. The empirical formula of the tin(II) hydroxide chloride precipitate in the range of pH 1.9 to 2.5 was determined to be  $2\text{SnO} \cdot \text{SnCl}_2 \cdot \text{H}_2\text{O}$ , and the empirical formula of the hydroxide obtained in the range of pH 7.0 to 7.7 was  $3\text{SnO} \cdot 2\text{H}_2\text{O}$ .

The composition of the tin(II) hydroxide chloride as well as the tin(II) hydroxide was determined by thermal analysis. The mean values of the respective results are listed in column 2 of Table A-53. Reliable analyses of tin(II) hydroxide chloride are obviously rather difficult to carry out, thus the question arises whether thermal analysis qualifies for this purpose.

Table A-53: Composition of tin(II) hydroxide chloride [1984ICH/TAK].

Composition	Exp.	$2\text{SnO} \cdot \text{SnCl}_2 \cdot \text{H}_2\text{O}$	$3\text{SnO} \cdot \text{SnCl}_2 \cdot 3\text{H}_2\text{O}$ [1963DON/MOS]	$\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{cr})$ abhurite
w ( $\text{SnCl}_2$ )	37.24%	39.75%	29.27%	44.69%
w ( $\text{SnO}$ )	58.72%	56.48%	62.39%	51.59%
w ( $\text{H}_2\text{O}$ )	4.04%	3.78%	8.34%	3.72%

The same argument applies when Ichiba and Takeshita's thermo-analytical results on tin(II) hydroxide oxide are compared with the predicted formulae, see Table A-54.



Table A-54: Composition of tin(II) hydroxide oxide [1984ICH/TAK].

Composition	Exp.	3SnO·2H <sub>2</sub> O	5SnO·2H <sub>2</sub> O	3SnO·H <sub>2</sub> O
			[1961DON/MOS]	[1968HOW/MOS]
w(SnO)	92.72%	91.81%	94.92%	95.73%
w(H <sub>2</sub> O)	7.86%	8.19%	5.08%	4.27%

**[1984KOC/TOP]**

Based on the paper [1983TOP/KOC], additional experimental data and standard data of several books and reviews (listed in a table) a standard Gibbs energy of formation of SnS<sub>2</sub> was derived:

– 43.20 kcal·mol<sup>-1</sup> (– 180.75 kJ·mol<sup>-1</sup>) for good crystallised solids

– 41.30 kcal·mol<sup>-1</sup> (– 172.80 kJ·mol<sup>-1</sup>) for nearly amorphous SnS<sub>2</sub>.

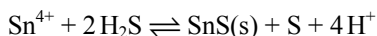
Also  $\Delta_f G_m^0(\text{SnCl}_6^{2-}, 298.15 \text{ K}) = -204.08 \text{ kcal}\cdot\text{mol}^{-1}$  (= – 856.88 kJ·mol<sup>-1</sup>) was derived from the model.

Table A-55: Experimental data on the solubility of SnS<sub>2</sub> at 25 °C and 1 bar H<sub>2</sub>S.

$m_{(\text{HCl})}/\text{mol}\cdot\text{kg}^{-1}$	$m_{(\text{Sn})} \times 100/\text{mol}\cdot\text{kg}^{-1}$	$m_{(\text{HCl})}/\text{mol}\cdot\text{kg}^{-1}$	$m_{(\text{Sn})} \times 100/\text{mol}\cdot\text{kg}^{-1}$
1.20	$4.30 \times 10^{-3}$	4.29	5.16
1.84	$1.75 \times 10^{-2}$	4.64	8.35
3.78	1.30	4.88	11.01
4.05	3.13	5.12	13.05

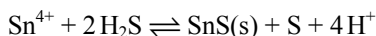
The standard Gibbs energy of formation of the sulfide ion used for the calculations is too small (91.88 kJ·mol<sup>-1</sup>). Data for the complete series of tin(IV) complexes are given without detailed information how the values have been obtained (Table A-56).

All formation data of complexes are 50 to 100 kJ·mol<sup>-1</sup> more negative than those selected by this review. In their previous paper [1983TOP/KOC] the authors mention formation of elemental sulfur during precipitation of SnS<sub>2</sub>. This reaction



is accompanied by formation of the much more soluble SnS. Thus the more negative formation Gibbs energies of chlorido complexes are required to adapt the data in the model. Simulations using the selected data confirm that this reaction will proceed.

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is accompanied by formation of the much more soluble SnS. Thus the more negative formation Gibbs energies of chlorido complexes are required to adapt the data in the model. Simulations using the selected data confirm that this reaction will proceed.

Table A-56: Comparison of formation data used by [1984KOC/TOP] and selected data of this review.

Species	$\Delta_f G_m^\circ$ (298.15 K)/ kcal·mol <sup>-1</sup>	$\Delta_f G_m^\circ$ (298.15 K)/ kJ·mol <sup>-1</sup>	$\Delta_f G_m^\circ$ (298.15 K)/ kJ·mol <sup>-1</sup>	$\Delta_f G_m^\circ$ (298.15 K)/ kJ·mol <sup>-1</sup> selected in this review
Sn <sup>4+</sup>	-0.59	-2.469	-2.469	46.711
SnCl <sup>3+</sup>	-35.40	-148.11	-14.473	-90.491
SnCl <sub>2</sub> <sup>2+</sup>	-70.92	-296.73	-31.925	-221.706
SnCl <sub>3</sub> <sup>+</sup>	-105.43	-441.12	-45.147	not existent
SnCl <sub>4</sub> (aq)	-137.73	-576.26	-49.119	-484.142
SnCl <sub>5</sub> <sup>-</sup>	-171.47	-717.43	-59.121	-615.359
SnCl <sub>6</sub> <sup>2-</sup>	-204.08	-853.87	-64.393	-746.576

Calculating  $\Delta_r G_m^\circ$  of the complexation reactions with the authors formation data and recalculating  $\Delta_f G_m^\circ$  of the complexes with  $\Delta_f G_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) = 0.67 \text{ kJ}\cdot\text{mol}^{-1}$  using the auxiliary formation data ( $\Delta_f G_m^\circ(\text{Cl}^-, 298.15 \text{ K}) = -131.217 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f G_m^\circ(\text{Sn}^{2+}, 298.15 \text{ K}) = -27.39 \text{ kJ}\cdot\text{mol}^{-1}$  (this review) as well as  $\Delta_f G_m^\circ = 28.54 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$  with  $\log_{10} K (298.15 \text{ K}) = -5.0$  [1999LOT/OCH] gives the values in column “new  $\Delta_f G_m^\circ (298.15 \text{ K})$ ”.

#### [1984PRE/RUE]

<sup>119</sup>Sn and <sup>195</sup>Pt NMR were used to characterise a number of cis-[MCl<sub>x</sub>(SnCl<sub>3</sub>)<sub>y</sub>]<sup>2-x-y</sup> complexes (M = Pd<sup>2+</sup>, Pt<sup>2+</sup>).

#### [1985DJO/ZMB]

Potentiometric titrations using a fluoride selective electrode were performed under inert atmosphere at 295.15 K in aqueous NaClO<sub>4</sub> solutions ( $I = 0.1, 0.5$  and  $1.0 \text{ M}$ ) and in water-ethanol mixture in order to determine the formation constants of the tin(II)-fluorido complexes at pH 5 ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.05 \text{ mM}$ ). In aqueous solutions the formation of SnF<sub>q</sub><sup>2-q</sup> complexes with  $q = 1, 2, 3$  are reported. In 50 and 75% water-ethanol mixtures complexes with  $q = 1$  to 6 were detected. The experimental work seems to have been

done carefully. The hydrolysis of tin(II) was neglected during the evaluation of experimental data, due to the low tin(II) concentration applied. Although this assumption is not correct, in the concentration range used to determine  $\log_{10} \beta_1$  ( $[F^-]_{\text{tot}} = 0.3$  to  $0.7$  mM,  $[F^-]_{\text{tot}}/[Sn^{2+}]_{\text{tot}} = 6$  to  $14$ ) the effect of the hydrolysis is probably not very large. The experimental data were evaluated graphically. This method works reasonably well for the determination of  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$ , but seems to fail for the higher complexes. In aqueous solutions  $K_2 < K_3$  for all ionic strengths applied. In addition,  $K_2 < K_3 \sim K_4 \sim K_5 \sim K_6$  was reported for 50 and 75% water-ethanol mixture. Therefore an uncertainty of  $\pm 0.3$  was assigned to the  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$  values, and  $\pm 0.6$  to  $\log_{10} \beta_3$ .

### [1985MAT/EVA]

Abhurite is a new mineral species found in blister-like protuberances on the surface of tin ingots submerged in a shipwreck about 100 years ago. X-ray-precession patterns show that the crystals are rhombohedral, space group  $R3m$ ,  $R3m$  or  $R32$ , and commonly twinned on (0001). Results of the chemical analysis conform well to the formula  $Sn_3O(OH)_2Cl_2$ . Different formulae have been ascribed to tin(II) chloride-hydroxide-oxide phases which had been prepared previously but none of them appeared to be identical with abhurite. Synthetic crystals prepared according to the procedure given in [1963DON/MOS], however, produced an X-ray pattern nearly identical to that of abhurite.

Matzko *et al.* report of a few other cases where basic tin(II) chlorides were found on tin ingots exposed to marine waters or buried in soil.

A comparison of the experimentally determined composition with the required ones in Table A-57 shows that the analytical data conform almost equally well to the correct formula of abhurite and the one suggested by the authors.

Table A-57: Composition of tin(II) chloride hydroxide oxide [1985MAT/EVA].

Composition	$Sn_3O(OH)_2Cl_2^\dagger$	$Sn_{21}Cl_{16}(OH)_{14}O_6(\text{cr})$ abhurite
w(Sn)	73.4 (74.65)%	73.45%
w(Cl) <sup>‡</sup>	15.7 (14.86)%	16.71%
w(O)	11.0 (10.06)%	9.43%
w(H)	0.4 (0.42)%	0.42%

<sup>†</sup> The stoichiometrically required composition is given in parenthesis

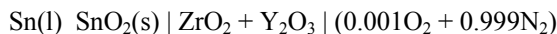
<sup>‡</sup> On the basic tin(II) chloride, synthesised according to [1963DON/MOS], 16.9% Cl was determined.

**[1986BAN]**

Although the equilibrium:



was studied many times using various techniques (see Table A-58), Bannister [1986BAN] used a novel reference electrode and studied Reaction (A.78) using potential measurements on the solid-electrolyte oxygen-concentration cell:



with a reference electrode of  $\{\text{Pt} + (\text{U}_{0.38}\text{Sc}_{0.62})\text{O}_{2 \pm x}\}$  powder and, separately, a conventional porous Pt reference electrode. Between 673 and 1167 K,  $\Delta_r G_m^\circ$  ((A.78),  $T$ ) =  $-(571.4 + 0.2030 T) \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$ . Third-law analysis of the results gives  $\Delta_r H_m^\circ$  (A.78) =  $-(578.0 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$ , in good agreement with the most recent calorimetric determination.

Table A-58: Values of the standard molar Gibbs energy change  $\Delta_r G_m^\circ$  ((A.78),  $T$ )/ $\text{kJ}\cdot\text{mol}^{-1} = A + B(T/\text{K})$  obtained from the literature. The information in brackets indicates the reactive gas mixture or reference electrode used. Table modified from [1986BAN] with several additions.

Reference	$T/\text{K}$	Technique	A/ $\text{kJ}\cdot\text{mol}^{-1}$	B/ $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_r G_m^\circ$ (1000 K)/ $\text{kJ}\cdot\text{mol}^{-1}$
[1956PLA/MEY]	806 – 1107	Gas equilibrium (CO + CO <sub>2</sub> )	– 581.0	0.2112	– 369.8
[1960ATA/UTA]	973 – 1148	Gas equilibrium (H <sub>2</sub> + H <sub>2</sub> O)	– 572.6	0.2032	– 369.4
[1965BEL/ALC]	773 – 983	Solid-electrolyte (Ni + NiO)	– 585.6	0.2132	– 372.4
[1972OIS/HIR]	1173 – 1373	Solid-electrolyte (Ni + NiO)	– 562.6	0.1953	– 367.3
[1975PET/FAR]	773 – 1380	Solid-electrolyte (Ni + NiO)	– 578.6	0.2085	– 370.1
[1977SEE/STA]	990 – 1373	Solid-electrolyte (Ni + NiO)	– 577.4	0.2088	– 368.6
[1978RAM/BAR]	773 – 1173	Solid-electrolyte (Cu + Cu <sub>2</sub> O)	– 573.8	0.2035	– 370.3
[1978IWA/YAS]	1023 – 1273	Solid-electrolyte (Ni + NiO)	– 586.7	0.2144	– 372.3
[1982SUG/KUW]	773 – 1165	Solid-electrolyte (Pb + PbO)	– 574.2	0.2049	– 369.3
[1983KAR/THO]	1041 – 1351	Solid-electrolyte (Pt/O <sub>2</sub> )	– 579.7	0.210	– 369.7
[1983KAM/OST]	1073 – 1273	Solid-electrolyte (Pt/air)	– 576.6	0.2087	– 367.9
[1986BAN]	673 – 1167 (useful range)	Solid-electrolyte	– 571.4	0.2030	– 368.4
[1994YAN/SUI]	720 – 990		– 574.33	0.202	– 372.33
[2001MAL/EDW]	772 – 1206		– 568.9	0.200	– 368.9

The published gas compositions or cell potentials in Table A-58 have been converted to values of  $\Delta_r G_m^\circ$  using JANAF values for CO(g), CO<sub>2</sub>(g), H<sub>2</sub>O(g), Cu<sub>2</sub>O(s),

and PbO(s) [1971STU/PRO], [1974CHA/CUR]. For cell measurements employing (Ni + NiO) as the reference electrode, the values recommended by Rand [1982RAN] were used for  $\Delta_r G_m^0$  (NiO). Each set of values was fitted to a straight line of the form:

$$\Delta_r G_m^0 / \text{kJ} \cdot \text{mol}^{-1} = A + B(T/\text{K}). \quad (\text{A.79})$$

The values of  $\Delta_r G_m^0$  calculated from enthalpies and entropies were fitted to Eq. (A.79). These calculations used the JANAF tables for  $\text{O}_2(\text{g})$ , [1973HUL/DES] for Sn(s or l) and, for  $\text{SnO}_2(\text{c})$ : the standard molar enthalpy of formation from Lavut *et al.* [1981LAV/TIM] the standard entropy reported by Zhogin *et al.* [1980ZHO/KOS], high-temperature enthalpy and entropy increments calculated by Kelley [1960KEL] from the main results of Kapustinsky *et al.* [1936KAP/ZIL].

### [1986MAT/THI]

$^{119}\text{Sn}$  NMR studies of  $\text{Na}_4\text{P}_2\text{O}_7$  solutions containing  $\text{SnCl}_2$  ( $\text{P}_2\text{O}_7^{4-}/\text{Sn}$  ratio = 10:1) at pH 6 in presence of air indicate the formation of a stable Sn(IV)-pyrophosphate complex, showing a quintuplett at 675 ppm (relative to tetramethyltin). These results indicate the formation of a  $\text{Sn}(\text{P}_2\text{O}_7)_2^{4-}$  complex, with symmetrical coordination by four O-atoms.

### [1986TUR/KRA]

Potentiometric study, using tin amalgam and glass electrodes, was performed to determine the composition and stability constants of tin(II) complexes formed in the tin(II)-pyrophosphate system between pH = 7.1 to 12.0 in 1 M  $\text{NaClO}_4$  medium at 298 K under argon atmosphere. The concentration of the ligand varied between 2.8 and 70 mM, with constant tin(II) concentrations of 0.5 mM. Under these conditions the following complexes were detected:  $\text{SnP}_2\text{PO}_7^{2-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_2^{6-}$ ,  $\text{Sn}(\text{OH})(\text{P}_2\text{O}_7)^{3-}$ ,  $\text{Sn}(\text{OH})_2(\text{P}_2\text{O}_7)^{4-}$  and  $\text{Sn}(\text{OH})(\text{P}_2\text{O}_7)_2^{7-}$  and  $\text{Sn}(\text{OH})_3^-$ .

Only graphical presentation of the experimental data are provided. The complex  $\text{Sn}(\text{OH})_3^-$  is the predominant species in the solution above pH 10.5. The reported equilibrium constant for the reaction  $\text{Sn}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Sn}(\text{OH})_3^-$  is  $\log_{10} \beta_3 = (25.5 \pm 0.08)$ . The value of  $\text{pK}_w$  used by the authors is 13.8, thus the above equilibrium constant is equivalent with  $\log_{10} \beta_{3,1}^* = -(15.9 \pm 0.1)$ . This value is notably higher than it can be estimated from the SIT model using the other available data.

### [1986TUR/KRA2]

This is a continuation of the work reported in [1986TUR/KRA]. Potentiometric study, using tin amalgam and glass electrodes, was performed to determine the composition and stability constants of the complexes formed in the tin(II)-pyrophosphate system between pH = 1.8 to 7.0 in 1 M  $\text{NaClO}_4$  medium at 298 K under argon atmosphere. The concentration of the ligand varied between 20 and 70 mM, while the tin(II) concentration was 0.5 mM. Under these conditions the following complexes were

detected:  $\text{SnP}_2\text{O}_7^{2-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_2^{6-}$ ,  $\text{SnHP}_2\text{O}_7^-$ ,  $\text{SnH}_2\text{P}_2\text{O}_7(\text{aq})$ ,  $\text{SnH}(\text{P}_2\text{O}_7)_2^{5-}$ ,  $\text{SnH}_2(\text{P}_2\text{O}_7)_2^{4-}$ ,  $\text{SnH}_3(\text{P}_2\text{O}_7)_2^{3-}$  and  $\text{SnH}_4(\text{P}_2\text{O}_7)_2^{2-}$ . Similarly to [1986TUR/KRA] the complexation of pyrophosphate with sodium ion was not taken into account, therefore the equilibrium constants reported in [1986TUR/KRA2] can only be regarded as apparent formation constants (see also the discussion on [1991DUF/WIL]). The graphically presented experimental data were combined with those reported in [1986TUR/KRA], and were re-evaluated for the purposes of this review, to identify the composition of the formed complexes. The formation constants for the hydroxido complexes were calculated from the selected values of this review. The assumption of nine complexes is sufficient to reproduce fairly well the *c.a.* 200 experimental data (the species  $\text{SnH}_2\text{P}_2\text{O}_7(\text{aq})$  and  $\text{SnH}_4(\text{P}_2\text{O}_7)_2^{2-}$  were rejected). Although, most of the complexes were identified in [1991DUF/WIL], too, the speciation is rather different from that suggested in [1991DUF/WIL] (see Figure A-46).

### [1987TUR/KRA]

Polarographic method was used to determine the stability of pyrophosphato complexes of tin(II) in the pH range 0.90 to 4.45 under argon atmosphere (1 M  $\text{NaClO}_4$ , 25 °C). The concentration of the ligand varied between 1.8 and 70.0 mM, the tin(II) concentration was 0.1 mM. The cathodic reduction of tin(II) was found to be quasi-reversible. The authors reported the formation of identical complexes as in their earlier potentiometric study [1986TUR/KRA2]. The method devised by DeFord and Hume was used to calculate the formation constants of the complexes formed. The formation constants derived from the polarographic [1987TUR/KRA] and potentiometric [1986TUR/KRA2] data are in perfect agreement. The complexation of pyrophosphate with sodium ion was not taken into account, therefore this work has similar limitations to that discussed in [1986TUR/KRA] and [1986TUR/KRA2] (see also the discussion on [1991DUF/WIL]).

### [1989MAO/YOU]

$^{119}\text{Sn}$  NMR spectra of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  dissolved either in pure water ( $c_{\text{Sn(IV)}} = 0.7$  to 4.5 M) or in HCl solutions ( $c_{\text{Sn(IV)}} = 2.9$  M,  $c_{\text{HCl}} = 1$  to 12 M). Due to the high concentration of tin(IV) the complex  $\text{SnCl}_6^{2-}$  is the unique species only in 10 to 12 M HCl solutions ( $[\text{Cl}^-]_{\text{TOT}}/\text{Sn(IV)}_{\text{TOT}} > 7.4$ ). The observed resonances were assigned to the species  $\text{SnCl}_n(\text{H}_2\text{O})_{6-n}^{4-n}$  ( $n = 1$  to 6). Although, the authors mentioned the possible formation of hydroxido complexes, the aqua and hydroxido complexes were regarded equivalent.

### [1989MAO/YOU2]

Two-dimensional  $^{119}\text{Sn}$  exchange spectroscopy was applied to study the kinetics of hydrolysis of tin(IV)-chlorido complexes.  $^{119}\text{Sn}$  EXSY (exchange spectroscopy) spectra have been recorded for two solutions, 2 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was dissolved either in (i) 2  $\text{cm}^3$  water or (ii) 4 M HCl ( $c_{\text{Sn(IV)}} = 2.9$  M). The authors use the word hydrolysis for the reaction



*i.e.* even in solution (i) no hydroxido complexes were considered (or were treated equivalent with the aqua complexes). The authors detected magnetisation exchanges between the successively formed  $\text{SnCl}_n(\text{H}_2\text{O})_{6-n}^{4-n}$  ( $n = 1 - 6$ ) species, and reported equilibrium constants for the above reactions (in fact they are dissociation constants). Since the formation of mixed hydroxido complexes was neglected, these constants are not reliable.

#### [1990BEA/MEN]

The behaviour of Sn(II) and Sn(IV) was studied by polarography in  $\text{H}_2\text{O}$ -HF mixtures ( $w_{\text{HF}} = 2$  to 100%,  $[\text{Sn}^{2+}]_{\text{tot}} = 0.001$  M). At low mass fraction of HF ( $w_{\text{HF}} = 0.1$  to 2.0%) the species  $\text{SnF}_3^-$  is present in the solution. With increasing mass fraction of HF decreasing coordination number of tin(II) was detected. At  $w_{\text{HF}} = 2$  to 45% and 45 to 55% the complexes  $\text{SnF}_2(\text{aq})$  and  $\text{SnF}^+$  are the predominant species, respectively. Above  $w_{\text{HF}} = 55\%$  the coordination of  $\text{HF}_2^-$  is suggested by the authors. In presence of Sn(IV) the formation of  $\text{SnF}_6^{2-}$ ,  $\text{SnF}_5^-$  and  $\text{SnF}_3^+$  was reported with increasing mass fraction of HF. The reported complex formation processes in concentrated hydrogen-fluoride are fundamentally different from those in more dilute aqueous solutions, therefore the formation constants given in [1990BEA/MEN] were not considered any further.

#### [1990KOK/RAK]

Equilibria in Sn(II) salt (sulphate, chloride, perchlorate, fluoride) and in  $\text{KSnF}_3$ ,  $\text{NH}_4\text{SnF}_3$ , or  $\text{NH}_4\text{Sn}_2\text{F}_5$  solutions was studied as a function of  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$  concentration by  $^{119}\text{Sn}$  NMR. The NMR chemical shift as acid is added is explained. Regions of existence of Sn(II) chlorido and fluorido complexes are established. A scheme is proposed for hydrolysis and complexation processes in these solutions.

#### [1991DJO/ZMB]

In order to interpret the interaction between tin(II) and hippuric acid, the authors investigated the hydrolysis of tin(II) ion by pH-metric titrations in 0.5 M  $\text{NaClO}_4$  medium at 298 K ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.5$  to 10 mM). The evaluation of experimental data indicated the formation of  $\text{Sn}_3(\text{OH})_4^{2+}$  and  $\text{Sn}_2(\text{OH})_2^{2+}$ .

Although no experimental data are reported, the work seems to have been done correctly (the oxidation of tin(II) was checked with pirocatechol violet and found to be negligible, data obtained below pH 1.2 were neglected). The authors suggested the formation of  $\text{Sn}_2(\text{OH})_2^{2+}$  as a minor hydrolysis product, which was rejected by the reviewers based on the extensive data of [1958TOB] and [1976GOB] (see comment on [1958TOB]). However, the formation of the complex  $\text{Sn}_2(\text{OH})_2^{2+}$  represents only a few percent of the overall pH effect. Therefore the value reported for  $\log_{10} \beta_{4,3}^*$  is

considered in the present assessment, but the reviewers assigned higher uncertainty to this constant than was reported by the authors.

### [1991DUF/WIL]

The chemical speciation of tin(II)- and tin(IV)-pyrophosphate systems were investigated by a pH-metric method in 0.15 M NaCl solution at 25 °C under nitrogen atmosphere. The authors also determined the protonation constants of pyrophosphate under identical conditions. The hydroxido complexes of tin(II) and tin(IV) were taken into account during the calculations (the formation constants were taken from [1978KRA]), but only the species  $\text{Sn}(\text{OH})_3^-$  was formed in appreciable amount (above pH 8). The pH-metric curves were obtained at different pyrophosphate-tin(II) ratios and for different pyrophosphate (10 to 50 mM) and tin (3 to 25 mM) concentrations. The authors reported the formation of a white precipitate below pH 2.6 in the tin(II)-pyrophosphate system, which was identified as  $\text{Sn}_2\text{P}_2\text{O}_7(\text{s})$ . Similar observations were not reported in related publications [1980ORE/AND2], [1986TUR/KRA], [1986TUR/KRA2], [1987TUR/KRA], which is probably due to the higher concentration of tin(II) applied in [1991DUF/WIL]. The authors suggested the formation of seven Sn(II) complexes:  $\text{SnP}_2\text{O}_7^{2-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_2^{6-}$ ,  $\text{SnH}(\text{P}_2\text{O}_7)_2^{5-}$ ,  $\text{SnH}_2(\text{P}_2\text{O}_7)_2^{4-}$ ,  $\text{SnH}_3(\text{P}_2\text{O}_7)_2^{3-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_3^{10-}$  and  $\text{Sn}(\text{OH})(\text{P}_2\text{O}_7)^{3-}$ . Although several common species can be found, the speciation based on the data of Tur'yan *et al.* [1986TUR/KRA], [1986TUR/KRA2], [1987TUR/KRA] and that suggested by Duffield *et al.* are rather different (Figure A-46). This is due to the neglected  $\text{Na}^+ - \text{P}_2\text{O}_7^{4-}$  interaction and to the different experimental conditions used (Tur'yan *et al.* applied 1 M  $\text{NaClO}_4$  as background electrolyte and a notably wider range of tin(II)/pyrophosphate ratios).

In addition, the authors determined the solubility of  $\text{Sn}_2\text{P}_2\text{O}_7(\text{s})$ . The solid Sn(II) pyrophosphate (obtained from Unilever Research, U.K.) was not characterised. The equilibrium between the solid and the solution (pure water and 0.15 M (Na,H)Cl with different amount of HCl) phases was found to be reached within 7 hours. The dissolved tin was determined by atomic absorption spectroscopy. The formation of pyrophosphate complexes were taken into account during the calculation of solubility constants. The reported  $\log_{10} K_{s,0}$  values showed rather important pH dependence (see Table A-59).

The authors also reported the formation of very stable tin(IV)-pyrophosphate complexes ( $\text{SnHP}_2\text{O}_7^+$ ,  $\text{SnHP}_2\text{O}_7(\text{aq})$ ,  $\text{SnH}(\text{P}_2\text{O}_7)_2^{3-}$ ,  $\text{Sn}(\text{P}_2\text{O}_7)_2^{4-}$ ,  $\text{SnH}_{-1}(\text{P}_2\text{O}_7)_2^{5-}$ ), which prevents the precipitation of hydrated  $\text{SnO}_2(\text{s})$  ion in the whole pH-range studied (pH = 2 to 10). Among the water soluble hydroxido complexes  $\text{Sn}(\text{OH})_5^-$  and  $\text{Sn}(\text{OH})_6^{2-}$ , only the latter was considered in the calculations ( $\log_{10} \beta_{6,1}^* = -24.1$ , taken from [1978KRA]), and it was found to be dominant above pH 8.3 (however, at this pH the complex  $\text{Sn}(\text{OH})_5^-$  should be the dominant species in solution, based on the selected values for the alkaline hydrolysis of tin(IV), see chapter VII.1.2).



Figure A-46: Speciation curves in the tin(II)-pyrophosphate system ( $[\text{Sn}^{2+}]_{\text{T}} = 10^{-4} \text{ M}$ ,  $[\text{PO}_4^{3-}]_{\text{T}} = 10^{-3} \text{ M}$ ,  $T = 298 \text{ K}$ ). a) curves calculated using the data reported in [1991DUF/WIL] for  $I = 0.15 \text{ M NaCl}$ , b) speciation suggested by Tur'yan *et al.* [1986TUR/KRA], [1986TUR/KRA2], [1987TUR/KRA] for  $I = 1.0 \text{ M NaClO}_4$ .

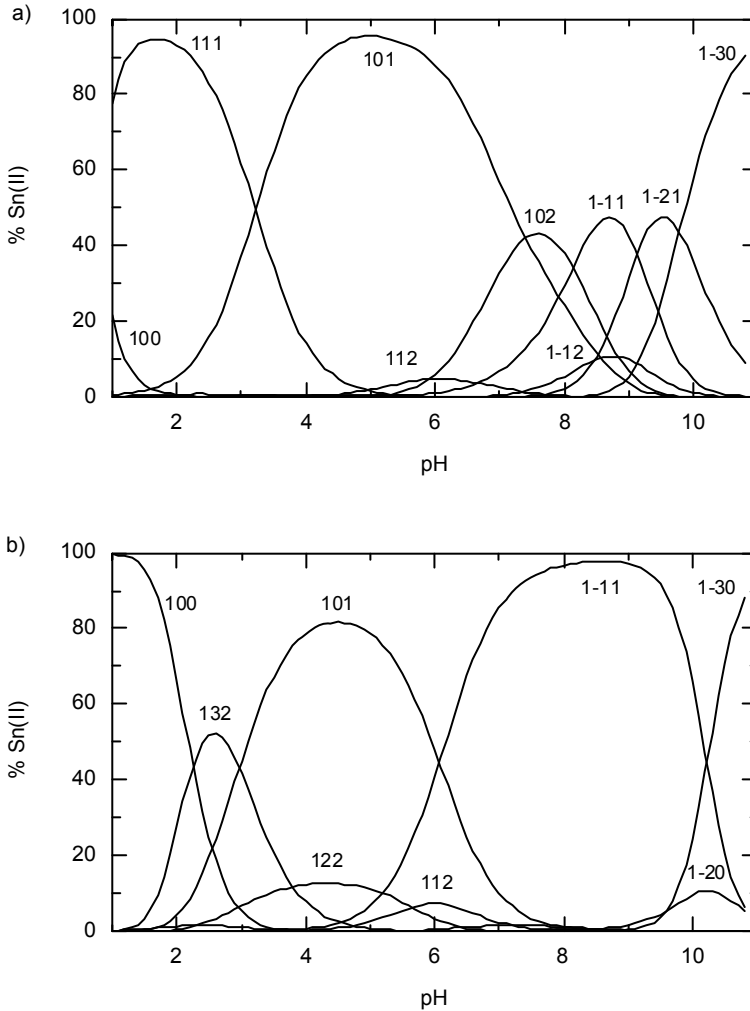


Table A-59: The solubility constant of  $\text{Sn}_2\text{P}_2\text{O}_7(\text{s})$  reported in [1991DUF/WIL] for different ionic media.

Composition of the solution	pH at the equilibrium	$\log_{10} K_{s,0}$
100 mM HCl + 50mM NaCl	1.07	$-20.33 \pm 0.24$
50 mM HCl + 100 mM NaCl	1.39	$-20.08 \pm 0.20$
10 mM HCL + 140 mM NaCl	1.86	$-20.00 \pm 0.10$
5 mM HCl + 145 mM NaCl	2.22	$-19.54 \pm 0.09$
1 mM HCl + 149 mM NaCl	2.76	$-19.12 \pm 0.12$
150 mM NaCl	3.32	$-18.29 \pm 0.05$
water	3.26	$-19.15 \pm 0.08$

**[1991GUR/VEY]**

A detailed and up-to-date review and critical evaluation of the experimental data on thermodynamic properties of tin,  $\text{SnS}$  and  $\text{SnS}_2$ . Properties include: phases, structure, heat capacity of solid, liquid and gas as functions of temperature, enthalpies and temperatures of transition, enthalpies of solid, liquid and gas, standard and temperature-dependent entropies, Gibbs energy function. Special attention is given to evaluating enthalpies of formation and experimental methods. This reference, together with [1973HUL/DES], represents the most complete and authoritative critical evaluation to date of thermodynamic properties of tin element.

This reference, together with [1974MIL], similarly represents the most complete and authoritative critical evaluation to date of thermodynamic properties of  $\text{SnS}$  and  $\text{SnS}_2$ .

Gurvich and Veyts' review on the oxides is summarised in Table A-60.

Gurvich and Veyts summarised the experimental data on tin bromides as shown in Table A-61.

Calorimetric data on  $\text{SnI}_2(\text{cr})$  and  $\text{SnI}_4(\text{cr})$  as summarised by Gurvich and Veyts are shown in Table A-62 and Table A-63.

Table A-60: Review by Gurvich and Veyts [1991GUR/VEY] of the results of the determination of  $\Delta_f H_m^o$  (SnO<sub>2</sub>, cr, 298.15 K).

Reference	Method	$\Delta_f H_m^o / \text{kJ} \cdot \text{mol}^{-1}$	
		2 <sup>nd</sup> Law	3 <sup>rd</sup> Law
[1928EAS/ROB]	Investigation of reaction equilibrium $\frac{1}{2}\text{Sn(l)} + \text{H}_2\text{O(g)} \rightleftharpoons \frac{1}{2}\text{SnO}_2(\text{cr}) + \text{H}_2(\text{g})$ by dynamic technique, 928 – 1082 K, 3 points.	$-586 \pm 15$	$-574.8 \pm 3.0$
	The same, static technique, 1046 – 1169 K, 7 points.	$-571 \pm 12$	$-575.4 \pm 1.5$
	Investigation of reaction equilibrium $\frac{1}{2}\text{Sn(l)} + \text{CO}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{SnO}_2(\text{cr}) + \text{CO(g)}$ by dynamic technique, 918 – 1088 K, 6 points.	$-599 \pm 10$	$-581 \pm 1.5$
[1932MEY/SCH]	The same, dynamic technique, 882 – 1061 K, 12 points	$-582.2 \pm 2.5$	$-579.9 \pm 1.5$
[1936KAP/ZIL]	The same, static technique, 973 – 1280 K, 12 points	$-591 \pm 5$	$-577.3 \pm 1.5$
[1937KLA]	The same, 773 – 1073 K, 4 points	$-580.5 \pm 3.0$	$-580.3 \pm 2.0$
[1956PLA/MEY]	The same, circulation technique, 806 – 1007 K <sup>a</sup>	$-581.8 \pm 2.5$	$-579.9 \pm 1.5$
[1929MAI]	Potential measurements on the reactions involved SnO <sub>2</sub> (cr), $\Delta_f G_m^o$ (SnO <sub>2</sub> , cr, 298.15 K) = $-515.5$	–	$-577.3 \pm 1.0$
[1965BEL/ALC]	Potential measurements on the reactions involved solid electrolyte, $\text{Sn(l)} + \text{O}_2(\text{g}) \rightleftharpoons \text{SnO}_2(\text{cr})$ , 770 – 980, 7 points	$-586$	$-581.9 \pm 1.0$
[1966MAT/GOT]	The same, 773 – 1373 K	$-566$	$-576.5$
[1975PET/FAR]	The same, 773 – 1380 K, 14 points	$-579.3$	$-579.3 \pm 1.0$
[1977SEE/STA]	The same, 990 – 1370 K	$-579.1$	$-(577.8 \pm 1.0)$
[1933EMM/SCH]	Investigation of reaction equilibrium $\frac{1}{2}\text{SnO}_2(\text{cr}) + \text{H}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{Sn(l)} + \text{H}_2\text{O(l)}$ by dynamic technique, 973 – 1073 K, 4 points	$-579.8 \pm 5.0$	$-580.0 \pm 1.5$
[1938ISH/AND]	The same, static technique, 894 – 1076 K, 12 points	$-584.6 \pm 2.0$	$-580.7 \pm 1.5$
[1960ATA/UTA]	The same, dynamic technique, 973 – 1148 K, 9 points	$-(575 \pm 5)$	$-579.9 \pm 1.0$
[1938ISH/AND]	Investigation of reaction equilibria $\frac{1}{2}\text{SnO}_2(\text{cr}) + \text{D}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{Sn(l)} + \text{D}_2\text{O(g)}$ , 923 – 1093 K, 12 points	$-582.5 \pm 2.0$	$-583.0 \pm 1.5$
[1953HUM/OBR]	Calorimetric, combustion of tin in oxygen	$-580.78 \pm 0.40$	
[1979LAV/TIM],	The same	$-577.63 \pm 0.20$	
[1981LAV/TIM]			

Table A-61: Results of the determination of  $\Delta_f H_m^0$  (SnBr<sub>4</sub>, cr, 298.15 K).

Reference	Method	$\Delta_f H_m^0$ (SnBr <sub>4</sub> , cr, 298.15 K)/ kJ·mol <sup>-1</sup>
[1898HER]	Calorimetric, $\beta\text{-Sn} + 2\text{Br}_2(\text{l}) \rightleftharpoons \text{SnBr}_4(\text{cr})$ <sup>(a)</sup>	- 391.1
[1975MIK/JAN]	Calorimetric, $\beta\text{-Sn} + 2\text{Br}_2(\text{l}) \rightleftharpoons \text{SnBr}_4(\text{cr})$ , dissolution of Br <sub>2</sub> , Sn, and SnBr <sub>4</sub> in CS <sub>2</sub>	- 386.1 ± 2.0
[1977STE/KOK]	Calorimetric, $\beta\text{-Sn} + 2\text{Br}_2(\text{l}) \rightleftharpoons \text{SnBr}_4(\text{cr})$ . The enthalpies of reactions of Sn, Br <sub>2</sub> and SnBr <sub>4</sub> with a solution of bromine in CCl <sub>4</sub> were measured.	- 390.2 ± 1.7

a To calculate this value, the enthalpy of dissolution of SnBr<sub>4</sub> in water was used.

Table A-62: Results of the determination of  $\Delta_f H_m^0$  (SnI<sub>2</sub>, cr, 298.15 K).

Reference	Method	$\Delta_f H_m^0$ (SnI <sub>2</sub> , cr, 298.15 K)/ kJ·mol <sup>-1</sup>
[1878BER]	Calorimetric $\text{SnCl}_2(\text{cr}) + 2\text{KI}(400\text{H}_2\text{O}) \rightleftharpoons \text{SnI}_2, \text{cr} + 2\text{KCl}(400\text{H}_2\text{O})$ .	- 154.2
[1973MIK]	Calorimetric, $\beta\text{-Sn} + \text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_2(\text{cr})$ , dissolution of I <sub>2</sub> , Sn, and SnI <sub>2</sub> in CS <sub>2</sub> .	- 154.3 ± 2.0
[1976CAR/WOO]	Calorimetric, $\beta\text{-Sn} + \text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_2(\text{cr})$ ; The measurement details not reported.	- 143.9 ± 3.6
[1977STE/KOK]	Calorimetric, $\beta\text{-Sn} + \text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_2(\text{cr})$ . The enthalpies of reactions of Sn, I <sub>2</sub> and SnI <sub>2</sub> with a solution of iodine in CCl <sub>4</sub> were measured.	- 152.1 ± 2.0

Table A-63: Results of the determination of  $\Delta_f H_m^0$  (SnI<sub>4</sub>, cr, 298.15 K).

Reference	Method	$\Delta_f H_m^0$ (SnI <sub>4</sub> , cr, 298.15 K)/ kJ·mol <sup>-1</sup>
[1973MIK]	Calorimetric, $\beta\text{-Sn} + 2\text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_4(\text{cr})$ . The enthalpies of reactions of dissolution of I <sub>2</sub> , Sn, and SnI <sub>4</sub> in ethyl acetate were measured.	- 214.3
	Calorimetric, $\beta\text{-Sn} + 2\text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_4(\text{cr})$ , dissolution of I <sub>2</sub> , Sn and SnI <sub>4</sub> in CS <sub>2</sub>	- 208.8 ± 2.0
[1976CAR/WOO]	Calorimetric, $\beta\text{-Sn} + 2\text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_4(\text{cr})$ . The enthalpies of reactions with solution of FeCl <sub>3</sub> in HCl were measured.	- 215.3 ± 2.3
[1977STE/KOK]	Calorimetric, $\beta\text{-Sn} + 2\text{I}_2(\text{cr}) \rightleftharpoons \text{SnI}_4(\text{cr})$ . The enthalpies of reactions of Sn, I <sub>2</sub> and SnI <sub>4</sub> with solution of iodine in CS <sub>2</sub> were measured.	- 206.1 ± 2.0

**[1991GUR/VEY2]**

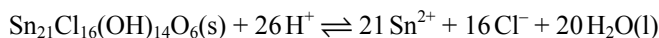
Companion volume to [1991GUR/VEY]. Contains tables of recommended values of elemental tin (from 100 to 5000 K), SnS (from 100 to 6000 K) and SnS<sub>2</sub> (from 100 to 6000 K) according to evaluations in [1991GUR/VEY].

**[1991KHR/ZAP]**

Mössbauer spectral parameters were used to estimate the speciation of 0.05-0.01M SnCl<sub>4</sub> in 0.2 to 1 M HCl solutions. The identified mixed complexes are SnCl<sub>5</sub>(OH)<sup>2-</sup>, SnCl<sub>4</sub>(OH)<sub>2</sub><sup>2-</sup>, SnCl<sub>3</sub>(OH)<sub>3</sub><sup>2-</sup> and SnCl<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup>. For example, the two major species (≈ 30-35%) in 1 M HCl solution of tin(IV) are the complexes SnCl<sub>4</sub>(OH)<sub>2</sub><sup>2-</sup> and SnCl<sub>3</sub>(OH)<sub>3</sub><sup>2-</sup>.

**[1992EDW/GIL]**

The true formula of abhurite is Sn<sub>21</sub>Cl<sub>16</sub>(OH)<sub>14</sub>O<sub>6</sub>. Basic tin(II) chloride was synthesised following two reported methods [1963DON/MOS] and [1984ICH/TAK]. Its powder diffraction patterns were found identical with the mineral abhurite. A solubility constant for this phase was determined at 298.15 K. For the reaction



$\log_{10} {}^*K_{s,162026} = - (31.9 \pm 0.7)$  was found. The uncertainty assigned is  $1\sigma$ .

The concentrations of Sn<sup>2+</sup> and Cl<sup>-</sup> given in Table A-64 were calculated by the authors using the COMICS program and stability constants for chlorido and hydroxido complexes of tin(II) and sodium ions from [1976BAE/MES] and [1976SMI/MAR].

Table A-64: Experimental and derived results for dissolution of abhurite at 298.2 K.

1000·[Sn <sup>2+</sup> ]/M	10·[Cl <sup>-</sup> ]/M	<i>I</i> /M	pH (molar basis)
8.471	4.163	0.390	1.184
8.037	4.198	0.390	1.199
7.061	4.286	0.390	1.281
6.530	4.341	0.390	1.281
6.681	4.294	0.390	1.305
4.812	4.533	0.400	1.330
5.020	4.490	0.400	1.350

For converting these results to the molality basis, see Table A-65, the ionic medium was considered to consist of *I* M NaCl (*m/c* = 1.00975, interpolated according to Table II-5) and [Sn<sup>2+</sup>] as well as [Cl<sup>-</sup>] were accepted as listed above (Table 2 of [1992EDW/GIL]).

Table A-65: Experimental and derived results for dissolution of abhurite at 298.2 K converted to the molality basis.

$\log_{10}(m_{\text{Sn}^{2+}}/m)$	$(m_{\text{Cl}^-}/m)$	$I/m$	pH (molal basis)
-2.068	-0.376	0.394	1.180
-2.091	-0.373	0.394	1.195
-2.147	-0.364	0.394	1.277
-2.181	-0.358	0.394	1.277
-2.179	-0.363	0.394	1.301
-2.313	-0.339	0.404	1.326
-2.295	-0.344	0.404	1.346

The re-evaluation of these data employing the SIT formalism showed that they are indeed consistent with the stoichiometry  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6(\text{s})$ , however, due to the narrow pH range the data would be consistent with  $\text{SnOHCl}\cdot\text{H}_2\text{O}(\text{s})$  as well.

This results in the following solubility constant  $\log_{10}^* K_{\text{s},16202621} = -(1.58 \pm 0.07)$ . and leads to  $(1/21) \Delta_f G_m^\circ(\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6, \text{cr}, 298.15 \text{ K}) = -(362.68 \pm 0.49) \text{ kJ}\cdot\text{mol}^{-1}$ .

Table A-66: Experimental and derived results for dissolution of abhurite at 298.2 K converted to the molality basis and re-evaluated using the SIT formalism.

$\log_{10} a_{\text{Sn}^{2+}}$	$\log_{10} a_{\text{Cl}^-}$	$\gamma_{16202621}$	$\log_{10}^* K_{\text{s},16202621}$
-2.6419	-0.5303	-3.05135	-1.5907
-2.6641	-0.5270	-3.07099	-1.5917
-2.7185	-0.5198	-3.11994	-1.5392
-2.7514	-0.5143	-3.14857	-1.5678
-2.7424	-0.5194	-3.14353	-1.5330
-2.8844	-0.4975	-3.26876	-1.6273
-2.8669	-0.5019	-3.25466	-1.5885

### [1992SAS/SHO]

Correlations between standard partial molar entropies,  $S_m^\circ$ , of aqueous mono-, di-, and trivalent ions at 25 °C and 1 bar and effective electrostatic radii,  $r_e$ , calculated from the corresponding crystallographic radii,  $r_x$ , have been constructed for coordination numbers from 4 to 12. An expanded set of predicted entropies based on revised Shannon-Prewitt [1976SHA] crystallographic radii is provided. These correlations are generalised such that they can be applied to monoatomic aqueous ions of any charge,  $z$ , or coordination number,  $n$ .

For  $\text{Sn}^{2+}$  no  $S_m^\circ$  value can be predicted, because [1976SHA] doesn't list the respective  $r_x$  value. It is, however, possible to predict  $S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K})$ . The set of equations (A.80) to (A.85) will be used.

$$S_m^\circ / \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = M_{z,n} \cdot (z^2/r_c) + B_{z,n} \quad (\text{A.80})$$

$$M_{z,n}/\text{\AA} = - \{ [20 \cdot (n-4)/z] + 100 \} \quad (\text{A.81})$$

$$r_c/\text{\AA} = r_x/\text{\AA} + 0.94 \cdot z \quad (\text{A.82})$$

$$B_{z,n} = m_z \cdot n + b_z \quad (\text{A.83})$$

$$m_z = -4.37/z + 11.64 \quad (\text{A.84})$$

$$b_z = 59.73 \cdot z - 19.63 \quad (\text{A.85})$$

$\text{Sn}^{4+}$ :  $z = 4$ ,  $n = 6$ ,  $M_{z,n} = -110 \text{ \AA}$ ,  $r_c = 4.45 \text{ \AA}$ ,  $m_z = 10.55$ ,  $b_z = 219.29$ ,  $B_{z,n} = 282.59$

$$\begin{aligned} S_m^\circ(\text{Sn}^{4+}, 298.15 \text{ K}) &= - (112.92 \pm 4.89) \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= - (472.50 \pm 20.46) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}. \end{aligned}$$

The uncertainty has been estimated by taking twice the average of the difference between  $S_m^\circ$  and  $S_m^\circ(\text{calc.})$  listed in Table A-67.

Table A-67: Comparison of experimental and calculated standard partial molar entropies of cations.

cation	$n$	$z$	$r_x/\text{\AA}$	$r_c/\text{\AA}$	$m_z$	$b_z$	$M_{z,n}$	$B_{z,n}$	$S_m^\circ /$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$S_m^\circ(\text{calc.})/$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$ \Delta S_m^\circ $
$\text{Ag}^+$	6	1	1.15	2.09	7.27	40.10	-140.00	83.72	73.45 <sup>(a)</sup>	70.02	3.43
$\text{Li}^+$	6	1	0.76	1.70	7.27	40.10	-140.00	83.72	12.24 <sup>(a)</sup>	5.72	6.52
$\text{Na}^+$	6	1	1.02	1.96	7.27	40.10	-140.00	83.72	58.45 <sup>(a)</sup>	51.43	7.02
$\text{K}^+$	6	1	1.38	2.32	7.27	40.10	-140.00	83.72	101.20 <sup>(a)</sup>	97.80	3.40
$\text{Rb}^+$	6	1	1.52	2.46	7.27	40.10	-140.00	83.72	121.75 <sup>(a)</sup>	112.17	9.58
$\text{Cs}^+$	6	1	1.67	2.61	7.27	40.10	-140.00	83.72	132.10 <sup>(a)</sup>	125.85	6.24
$\text{Tl}^+$	6	1	1.50	2.44	7.27	40.10	-140.00	83.72	125.50 <sup>(b)</sup>	110.22	15.28
$\text{Sn}^{2+}$	6	2	1.18	3.06	9.46	99.83	-120.00	156.56	-16.70 <sup>(a)</sup>	-1.27	15.43
$\text{Pb}^{2+}$	6	2	1.19	3.07	9.46	99.83	-120.00	156.56	18.50 <sup>(a)</sup>	0.88	17.63
$\text{Zn}^{2+}$	6	2	0.74	2.62	9.46	99.83	-120.00	156.56	-109.80 <sup>(a)</sup>	-111.49	1.69
$\text{Cd}^{2+}$	6	2	0.95	2.83	9.46	99.83	-120.00	156.56	-72.80 <sup>(a)</sup>	-54.61	18.19
$\text{Hg}^{2+}$	6	2	1.02	2.90	9.46	99.83	-120.00	156.56	-36.19 <sup>(a)</sup>	-37.48	1.29
$\text{Cu}^{2+}$	6	2	0.73	2.61	9.46	99.83	-120.00	156.56	-98.00 <sup>(a)</sup>	-114.42	16.42
$\text{Mg}^{2+}$	6	2	0.72	2.60	9.46	99.83	-120.00	156.56	-137.00 <sup>(a)</sup>	-117.38	19.62
$\text{Ca}^{2+}$	6	2	1.00	2.88	9.46	99.83	-120.00	156.56	-56.20 <sup>(a)</sup>	-42.29	13.91
$\text{Sr}^{2+}$	6	2	1.18	3.06	9.46	99.83	-120.00	156.56	-31.50 <sup>(a)</sup>	-1.27	30.23

(Continued on next page)

Table A-67 (continued)

cation	<i>n</i>	<i>z</i>	<i>r<sub>s</sub></i> /Å	<i>r<sub>c</sub></i> /Å	<i>m<sub>z</sub></i>	<i>b<sub>z</sub></i>	<i>M<sub>z,n</sub></i>	<i>B<sub>z,n</sub></i>	<i>S<sub>m</sub><sup>o</sup></i> / J·K <sup>-1</sup> ·mol <sup>-1</sup>	<i>S<sub>m</sub><sup>o</sup></i> (calc.)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	Δ <i>S<sub>m</sub><sup>o</sup></i>
Ba <sup>2+</sup>	6	2	1.35	3.23	9.46	99.83	-120.00	156.56	8.40 <sup>(a)</sup>	33.28	24.88
Am <sup>2+</sup>	7	2	1.21	3.09	9.46	99.83	-130.00	166.015	-1.00 <sup>(c)</sup>	-9.49	8.50
Ni <sup>2+</sup>	6	2	0.69	2.57	9.46	99.83	-120.00	156.56	-131.80 <sup>(d)</sup>	-126.40	5.40
Cr <sup>3+</sup>	6	3	0.62	3.44	10.18	159.56	-113.33	220.66	-317.98 <sup>(e)</sup>	-317.36	0.62
Al <sup>3+</sup>	6	3	0.535	3.355	10.18	159.56	-113.33	220.66	-325.00 <sup>(a)</sup>	-348.79	23.79
U <sup>3+</sup>	6	3	1.025	3.845	10.18	159.56	-113.33	220.66	-188.17 <sup>(c)</sup>	-186.69	1.48
Np <sup>3+</sup>	6	3	1.01	3.83	10.18	159.56	-113.33	220.66	-193.58 <sup>(c)</sup>	-191.03	2.55
Pu <sup>3+</sup>	6	3	1.00	3.82	10.18	159.56	-113.33	220.66	-184.51 <sup>(c)</sup>	-193.95	9.44
Am <sup>3+</sup>	6	3	0.975	3.795	10.18	159.56	-113.33	220.66	-201.00 <sup>(c)</sup>	-201.31	0.31
Am <sup>3+</sup>	8	3	1.09	3.91	10.18	159.56	-126.67	241.03	-201.00 <sup>(f)</sup>	-211.43	10.43
U <sup>4+</sup>	6	4	0.89	4.65	10.55	219.29	-110.00	282.57	-416.89 <sup>(c)</sup>	-401.33	15.57
U <sup>4+</sup>	9	4	1.05	4.81	10.55	219.29	-125.00	314.22	-416.89 <sup>(f)</sup>	-425.02	8.13
Np <sup>4+</sup>	6	4	0.87	4.63	10.55	219.29	-110.00	282.57	-426.39 <sup>(c)</sup>	-408.17	18.22
Pu <sup>4+</sup>	6	4	0.86	4.62	10.55	219.29	-110.00	282.57	-414.53 <sup>(c)</sup>	-411.61	2.92
Am <sup>4+</sup>	6	4	0.85	4.61	10.55	219.29	-110.00	282.57	-406.00 <sup>(c)</sup>	-415.07	9.07
Zr <sup>4+</sup>	6	4	0.72	4.48	10.55	219.29	-110.00	282.57	-490.57 <sup>(g)</sup>	-461.42	29.15
Th <sup>4+</sup>	9	4	1.09	4.85	10.55	219.29	-125.00	314.22	-422.58 <sup>(h)</sup>	-410.67	11.91
Sn <sup>4+</sup>	6	4	0.69	4.45	10.55	219.29	-110.00	282.57		-472.50	

10.23

References: (a): [1989COX/WAG]; (b): [2005OLI/NOL]; (c): [2003GUI/FAN]; (d): [2005GAM/BUG]; (e): [1976DEL/HAL]; (f): [1992SAS/SHO]; (g): [2005BRO/CUR]; (h): [1982WAG/EVA].

This value can be compared with that obtained by the modified Powell and Latimer correlation, Appendix A entry [1951POW/LAT].

$$S_m^o / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 1.5 \cdot (R/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \cdot \ln(M/\text{g}\cdot\text{mol}^{-1}) + (156.84 \pm 0.26) \\ - (1237.62 \pm 2.14) \cdot z \cdot (\text{Å}/r_c)^2 \\ S_m^o (\text{Sn}^{4+}, 298.15 \text{ K}) = -(468 \pm 33) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Although the correlations of [1992SAS/SHO] and [1951POW/LAT] are completely different, the predictions of  $S_m^o$  (Sn<sup>4+</sup>, 298.15 K) are similar.

### [1992TAY/COD]

The <sup>119</sup>Sn NMR spectra were used to investigate the aquahalostannate(IV) complexes formed by SnCl<sub>4</sub>(aq) and SnBr<sub>4</sub>(aq) in aqueous and hydrohalic acid solutions. Characteristic chem. shifts were assigned to the complex cations [SnX(H<sub>2</sub>O)<sub>5</sub>]<sup>3+</sup>, [SnX<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> and [SnX<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup>, [SnX<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>], and the complex anions [SnX<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> and [SnX<sub>6</sub>]<sup>2-</sup> (where X = Cl or Br); including the pairs of cis/trans or



fac/mer isomers. The CPMAS spectra of crystalline solids containing  $[\text{SnX}_6]^{2-}$  and cis- or trans- $[\text{SnCl}_4(\text{H}_2\text{O})_2]$  assisted these assignments. The NMR data yielded quantitative estimates of the amounts of the various species in solution as a function of the tin concentration from  $0.1 \text{ mol}\cdot\text{dm}^{-3}$ , where the hydrated stannic ion,  $\text{Sn}^{4+}(\text{aq})$ , is predominant, to near saturation where auto-complexing results in complex anion formation. Soluble hydrolysis products for which OH-bridged structures are proposed were detected in solutions without added HCl or HBr and increase in amount when NaOH is introduced. Solutions containing excess NaOH reveal  $[\text{Sn}(\text{OH})_6]^{2-}$  which has a chemical shift of  $-590 \text{ ppm}$  and exhibits the Raman frequencies:  $552(\nu_1)$ ,  $425(\nu_2)$ ,  $290 \text{ cm}^{-1} (\nu_3)$ , appropriate for octahedral ( $O_h$ ) symmetry. The  $^{119}\text{Sn}$  NMR spectra of tin(IV) mixed halide aqueous solutions consisted of signals ranging from  $-600 \text{ ppm}$  ( $\text{H}_2\text{O}$  and  $\text{Cl}^-$  ligands) to  $-2000 \text{ ppm}$  ( $\text{Br}^-$  ligands), due to the series of species represented by  $\text{SnCl}_x\text{Br}_y(\text{H}_2\text{O})_z$  (where  $x + y + z = 6$ ), and can be interpreted by relating the chemical shift of the tin nucleus to the sum of ligand electronegativities in a given complex. The solvent extraction of tin halides from aqueous acid solution by diethyl ether or isobutyl methyl ketone was investigated and tin(IV) shown to be extracted in the form of both molecular  $[\text{SnX}_4(\text{H}_2\text{O})_2]$  and ion-pair  $\text{H}^+(\text{aq})[\text{SnX}_5(\text{H}_2\text{O})]^-$  complexes. These species can also be generated in solution by adding small amounts of water to  $[\text{SnX}_6]^{2-}$  in acetone. Conjoint use of NMR and Raman spectra enables the major species in these systems to be determined and allows the  $\nu(\text{Sn}-\text{X})$  symmetric stretching frequencies to be identified and assigned.

#### [1994STE/FOT]

The protonation of pyrophosphate and triphosphate have been studied by potentiometry in  $(\text{CH}_3)_4\text{NCl}$ , NaCl and KCl ( $I = 0$  to  $0.75 \text{ M}$ ) and at different temperatures ( $t = 5$  to  $45 \text{ }^\circ\text{C}$ ). The authors reported reliable thermodynamic dissociation constants of pyrophosphoric acid.

#### [1994YAN/SUI]

The nonstoichiometry of tin oxides,  $\text{SnO}_{2-x}$ , was studied between  $694$  and  $990 \text{ K}$  by coulometric titration using solid state electrolytes (YSZ). The non-stoichiometry ( $x$ ) and the oxygen partial pressure ( $p_{\text{O}_2}$ ) are related via the proportionality  $x \sim p_{\text{O}_2}^{-1/6}$ . A phase  $\text{Sn}_3\text{O}_4$  has been formed between  $696$ - $731 \text{ K}$ . The Gibbs free energy change of formation of  $\text{Sn}_3\text{O}_4$  is given by  $\Delta_f G_m^\circ (\text{Sn}_3\text{O}_4)/\text{J}\cdot\text{mol}^{-1} = -1,163,960 + 417.36 (T/\text{K})$ .

#### [1994YAM/KAM]

Yamaguchi *et al.* [1994YAM/KAM] measured the high temperature heat content of SnSe over the temperature range of  $700$  to  $1550 \text{ K}$  using a drop calorimeter. They fitted their high temperature heat content data using a mathematical function (Shmate) and used the data on enthalpy of formation at  $298.15 \text{ K}$  ( $-90.8 \text{ kJ}\cdot\text{mol}^{-1}$ ) from Gadzhiev *et al.* [1960GAD/SHA] and the entropy of ( $89.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) from [1991KNA/KUB].

**[1995DJU/JEL]**

The hydrolysis of tin(II) ion has been studied in 3.0 M (Na)Cl medium at 298 K, by potentiometric titrations using a glass electrode. In the concentration range  $1.0 \leq c(\text{Sn}^{2+})/\text{mM} \leq 10.0$  and  $0.50 \leq -\log_{10} [c(\text{H}^+)/c^\circ] \leq 1.30$ , the experimental data were explained by the formation of the following complexes and their respective stability constants,  $(\log_{10} \beta_{p,q} \pm \sigma)$ :  $\text{Sn}_3(\text{OH})_4^{2+}$ ,  $-(2.70 \pm 0.01)$  and  $\text{SnOH}^+$ ,  $-(2.18 \pm 0.02)$ . These constants are much higher than those reported in 3 M  $\text{NaClO}_4$  (see comment on [1958TOB]), indicating that the hydrolytic processes strongly shifted toward the acidic region. Since the formation of  $\text{SnCl}_q^{2-q}$  complexes should retard the hydrolysis, the authors tried to explain this inconsistency by the highly asymmetric distribution of the electron density of the hybridised 5s orbital of tin(II), and by the role of chloride ion which “may aid in oxygen bonding to the tin by their electrostatic influence on H–OH bonds”. Although these speculations may be true (moreover the formation of the mixed hydroxido complex  $\text{Sn}(\text{OH})\text{Cl}(\text{aq})$  may result in a similar pH shift), the formation of  $\text{SnCl}_q^{2-q}$  complexes were not taken into account during the evaluation of experimental data, therefore the reported formation constants are not considered further in this review. From the experimental point of view the correct determination of hydrogen ion concentration between pH = 0.5 and 1.3 is doubtful using a glass electrode, and the experimental errors generated in this way may also explain the above mentioned inconsistency.

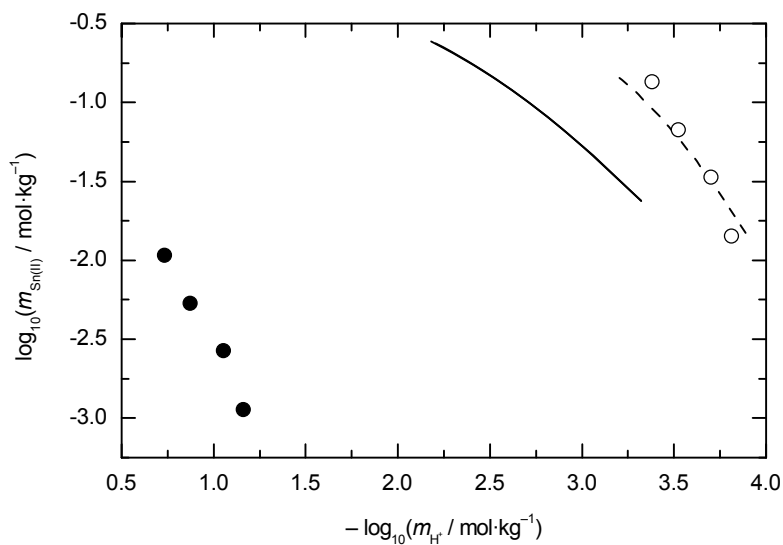
In addition, the solubility product of  $\text{Sn}(\text{OH})_2(\text{s})$  was determined from the hydrolytic curves,  $Z(-\log_{10} c(\text{H}^+))$  and found to be,  $\text{p}K_s = (27.9 \pm 0.1)$ . The hydrolytic precipitate was examined by elemental analysis, thermogravimetry, IR spectroscopy, X-ray powder diffraction and scanning electron microscopy. It was presumed that the main constituent of the precipitate can be formulated as  $\text{SnO} \cdot \text{H}_2\text{O}$ . This paper is particularly interesting, because the hydrolytic precipitate, presumably  $\text{SnO} \cdot \text{H}_2\text{O}$ , was characterised structurally. Comparison of the X-ray powder patterns, reported by the authors, with PDF files 01-084-2157 and 01-077-0452 of JCPDS indicates that the main constituent of the hydrolytic precipitate was  $\text{Sn}_6(\text{OH})_4\text{O}_4$ , hydroromarchite, but probably a minor amount of  $\text{SnO}_2$ , cassiterite, was also present, see Table A-68.

A recalculation shows that the solubility data of [1995DJU/JEL] neither agree with those predicted for abhurite,  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ , nor with those predicted for  $\text{SnO}$ , romarchite, see Figure A-47. By massive parallel displacement the experimental data coincide rather with the  $\text{SnO}$  solubility curve than with the abhurite one. This confirms the authors' implication that the hydrolytic precipitate contains no chloride. The low solubility of the hydrolytic precipitate may be related to its  $\text{SnO}_2$ , cassiterite, content, but no thermodynamic data can be derived.

Table A-68: Comparison of X-ray powder diffraction patterns with JCPDS.

SnO·H <sub>2</sub> O <i>d</i> /Å	[1995DJU/JEL] <i>i</i>	Sn <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> <i>d</i> /Å	01-084-2157 <i>i</i>	SnO <sub>2</sub> <i>d</i> /Å	01-077-0452 <i>i</i>
6.004	vw	5.97784	444		
5.624	vw	5.60509	381		
4.554	vw	4.55125	170		
3.533	w	3.53318	999		
3.379	w			3.36243	999
3.316	w	3.30330	594		
3.246	w				
2.986	w	2.98892	775		
2.810	s	2.79671	862		
2.621	w			2.65438	757
2.495	w	2.50667	368		
1.981	m	1.97963	24		

Figure A-47: Sn(OH)<sub>2</sub> solubility in 3.0 M NaCl (●: Experimental data of [1995DJU/JEL]; ○: parallel displaced data (x + 2.65, y + 11); solid line: calculated solubility of abhurite; dashed line: calculated solubility of SnO(cr)).

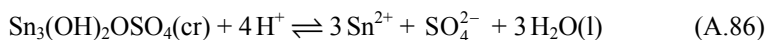


**[1996ABR/GRI]**

The structure of tin(II) hydroxide oxide,  $\text{Sn}_6\text{O}_4(\text{OH})_4$ , has been refined by Rietveld analysis of X-ray powder diffraction data. The structure was refined in the tetragonal space group  $P4_2c$  with  $a = 7.9268(4)$  Å and  $c = 9.1025(5)$  Å. This compound forms clusters of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  with the Sn atoms in distorted tetragonal pyramidal coordination geometries. Each Sn atom is coordinated to two bridging oxide O and two bridging hydroxy O atoms.

**[1996EDW/GIL]**

Tritin(II)dihydroxyoxosulfate (better tin(II) hydroxide oxide sulfate),  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ , is a rare corrosion product found on the surfaces of certain tin alloys. Solid  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$  has been synthesised by hydrolysis of  $\text{SnSO}_4$  in aqueous solutions in the range  $1.5 \leq \text{pH} \leq 2.6$ . The solubility constant in terms of Eq. (A.86) has been determined by measuring pH and activities of  $\text{Sn}^{2+}$  and  $\text{SO}_4^{2-}$  in solutions after 28 days equilibration with the solid phase. The measurements were carried out at 25 °C and  $I = 1.0$  M  $\text{NaClO}_4$ .



Inspection of Eq.(A.86) reveals that  $\log_{10} K_c = \log_{10} K_m$ , because  $\Sigma \nu_B = 0$ , see Eq. (II.38). Recalculation of the results listed in Table 3 of [1996EDW/GIL] resulted in a slightly different mean value, see Table A-69.

Table A-69: Recalculation of the results of [1996EDW/GIL] for the dissolution of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4(\text{cr})$ .

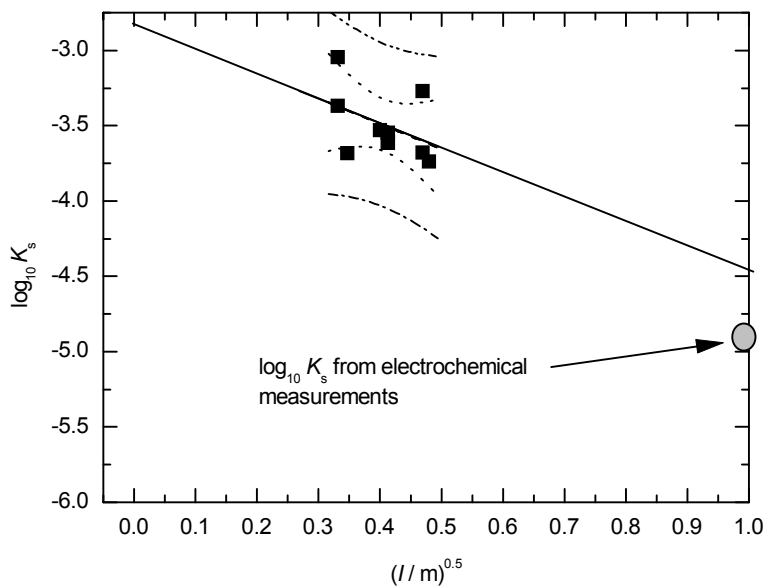
pH	$\log_{10} a_{\text{Sn}^{2+}}$	$\log_{10} a_{\text{SO}_4^{2-}}$	$\log_{10} a_{\text{H}_2\text{O}}$	$\log_{10} {}^*K_s$ (A.86)
1.595	-2.57	-3.48	-0.015	-4.855
1.570	-2.63	-3.44	-0.015	-5.095
1.567	-2.60	-3.20	-0.015	-4.777
1.507	-2.57	-3.50	-0.015	-5.227
1.479	-2.57	-3.24	-0.015	-5.079
			Mean value	-5.01 ± 0.37

Unfortunately, the paper does not allow to trace back the calibration procedure for activities of  $\text{Sn}^{2+}$ ,  $\text{SO}_4^{2-}$  in 1 M  $\text{NaClO}_4$ . Also the authors note (p. 430 footnote) on correcting the activity of sulfate for interference from tin activity is not clear.

In a number of additional equilibration experiments the tin content of the solutions were determined by AAS and the stoichiometric ionic strength had been calculated. From these results the concentration constant  $K$  for Eq. (A.86) can be calculated and plotted as a function of ionic strength (see Figure A-48). For comparison

the value from the electrochemical measurements is added,  $\log_{10} K$  from activities lies within the prediction limits from concentration measurements, which casts some doubts on the activity measurements also.

Figure A-48: Stoichiometric solubility constant for  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ .



### [1996PLY/GRE]

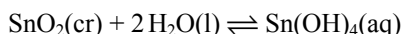
This is the key paper elucidating the application of the Pitzer as well as the Brønsted-Guggenheim-Scatchard specific ionic interaction models to the extrapolation of enthalpies of reaction in electrolyte systems to infinite dilution. The methods described in this paper became standard methods in the TDB projects.

For this review it is particularly important that the Vasil'ev [1967VAS] as well as the Vasil'ev and Yasinskii [1978VAS/YAS] approaches are criticised on the grounds that  $H_{2,I} = H_{2,I}^0 + \Phi_{L,i}$  is used instead of  $H_{2,I} = H_{2,I}^0 + L_{2,i}$ , where  $\Phi_{L,i}$  is the relative apparent molar enthalpy and  $L_{2,i}$  the relative partial molar enthalpy. Although the enthalpy of reaction at infinite dilution will probably not change very much, Vasil'ev *et al.*'s  $\Delta_r H_m^0$  have to be revised.

**[1997AMA/CHI]**

The solubility of SnO<sub>2</sub> was determined between pH 2 and 12 at 25 °C in an inert gas glove box. The oversaturation experiments were performed in 0.1 M NaClO<sub>4</sub>, using <sup>113</sup>Sn labelled tin(IV) chloride stock solutions. After the pH of the samples was adjusted to the desired values (pH = 2.1 to 11.9), the solutions were equilibrated for 1 or 6 months (the equilibrium needed less than 1 month). The concentration of tin(IV) in the liquid phase was determined by measuring the radioactivity of the solution. For the undersaturation measurements (*I* = 0.01 M NaClO<sub>4</sub>, pH = 1.9 to 7.8) crystalline SnO<sub>2</sub> was used, and the concentration of the dissolved tin(IV) was determined by ICP-MS. The results indicated considerably smaller solubility for the crystalline SnO<sub>2</sub> than for the amorphous oxide.

The solubility of crystalline SnO<sub>2</sub> according to the reaction



remains constant within  $1.9 \leq \text{pH} \leq 7.8$  and connects the aqueous hydroxido species of Sn(IV) in alkaline solution thermodynamically with the selected formation data of tin. One of the 7 data pairs measured in this pH range was an outlier and rejected by the reviewers. As the ionic medium was 0.01 M NaClO<sub>4</sub> no ionic strength correction has been applied to  $\log_{10} K_{s,0}(298.15 \text{ K}) = - (8.06 \pm 0.11)$ .

The experiments were performed very carefully, the applied methods for the determination of the concentration of dissolved tin(IV) are much more precise than those used in [1970BAR/KLI]. However, the authors made a mistake during the evaluation of the data in alkaline solutions, using wrong sign for the Davis equation. This error was corrected in a subsequent paper of the authors (see comments on [1998ODA/AMA]).

**[1997SAL/FER]**

The hydrolysis of Sn(II) has been studied in acidic solution by potentiometric method using two sensors (glass and tin-amalgam electrodes) at 25 °C and *I* = 3 M NaClO<sub>4</sub> ( $[\text{Sn}^{2+}]_{\text{tot}} = 0.24$  to  $2.03$  mM). The evaluation of the experimental data indicated the formation of Sn<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> and Sn(OH)<sup>+</sup>.

This work is similar to [1958TOB] and [1976GOB], aiming to solve the contradiction between the earlier reports ([1958TOB], [1964LIN/TU] and [1976GOB]) concerning the presence of Sn<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>. Salvatore *et al.* [1997SAL/FER] confirm the result of [1976GOB] and the re-evaluation of the combined datasets of [1958TOB] and [1976GOB] made by the reviewers (see comment on [1958TOB]).

Although the work seems to be done carefully, the experimental data reported in [1997SAL/FER] are somehow faulty, since even the graphical presentation of the data (Figure 1 in [1997SAL/FER]) could not be exactly reproduced.

**[1997SIP/CAP]**

The hydrolysis of Tl(I) has been studied at 25 °C using 205Tl-NMR spectroscopy and UV-Vis spectrophotometry in aqueous solutions with ionic strengths maintained by NaClO<sub>4</sub> at 2, 4, 6, and 8 M. The formation constant and the spectral characteristics for the hydroxido complex, TlOH (aq) have been determined. At high hydroxide ion concentrations there is clear evidence from the UV-Vis data for the formation of a Tl(OH)<sub>2</sub><sup>-</sup> species. The spectrum and an estimated formation constant for this second hydroxido complex are also reported.

**[1997VAS]**

Plyasunov and Grenthe's [1996PLY/GRE] criticism provoked a scientific controversy. Vasil'ev refutes Plyasunov and Grenthe's arguments. This controversy is of scientific interest for the TDB-Sn project.

**[1998ODA/AMA]**

This paper complements the solubility data reported in [1997AMA/CHI], using identical experimental methods (see comments on [1997AMA/CHI]). The solubility of amorphous SnO<sub>2</sub> in NaClO<sub>4</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, as well as in bentonite equilibrated systems were measured to investigate the influence of additional ligands present in the solution. No significant changes in solubility were observed in presence of Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>, as compared with the results obtained in NaClO<sub>4</sub> solution. On the other hand, in the bentonite equilibrated solutions the solubility of tin(IV) increased by two orders of magnitude. For the undersaturation experiments amorphous SnO<sub>2</sub>, formed during the oversaturated measurements, was applied. The authors used a selected dataset, based on the solubility data reported in [1997AMA/CHI] and those collected in this paper, to determine the solubility of amorphous SnO<sub>2</sub> in ≈ 0.1 M NaClO<sub>4</sub> solution (in Table 1 and 2, the authors reported erroneous ionic strength data, in reality the ionic strength was between 0.1 and 0.15 M; personal communication by Chie Oda).

The solubility data reported for  $I \approx 0.1$  M NaClO<sub>4</sub> were re-evaluated for the purposes of this review. Using the dataset selected by the authors, including 30 points from the oversaturation experiments (Figure VII-5, open squares),  $\log_{10} K_{s,0} = -(7.34 \pm 0.09)$ ,  $\log_{10} {}^* \beta_{5,1} = -(7.76 \pm 0.19)$  and  $\log_{10} {}^* \beta_{6,1} = -(18.14 \pm 0.15)$  can be calculated. However, this set does not include points between pH 8 and 10, where the complex Sn(OH)<sub>5</sub><sup>-</sup> dominates in the solution. Therefore, the re-evaluation included all experimental points, both over- and undersaturation data reported for  $I \sim 0.1$  M NaClO<sub>4</sub>. As it can be seen from Figure VII-5, the experimental data show good consistency, irrespective of the under- and oversaturated methods. The non-linear curve fitting resulted in the following equilibrium constants:  $\log_{10} K_{s,0} = -(7.22 \pm 0.08)$ ,  $\log_{10} {}^* \beta_{5,1} = -(8.38 \pm 0.25)$  and  $\log_{10} {}^* \beta_{6,1} = -(18.01 \pm 0.11)$ . These values were used to derive the selected thermodynamic constants. The uncertainties were increased by the reviewers, due to the fact that the actual ionic strength varied between 0.1 and 0.15 M.

**[1998PLY/GRE]**

Plyasunov and Grenthe's reply to [1997VAS] repeating the arguments put forward in [1998PLY/GRE].

The thermodynamic basis of the Plyasunov and Grenthe criticism is of considerable scientific interest.

**[1999LOT/OCH]**

This review provides thermodynamic data for predicting concentrations of Pd, Pb, Sn, Sb, Nb, and Bi in geologic environments, and contributes to an integration of the JNC (Japan Nuclear Cycle Development Institute) chemical thermodynamic database, JNC-TDB, for the performance analysis of geological isolation system of high level wastes. Besides treating hydrolysis in detail, this report focuses on the formation of complexes or compounds with chloride, fluoride, carbonate, nitrate, sulphate and phosphate. Other important inorganic ligands (sulphide for lead and antimony, ammonia for palladium) are also included. In this study, the specific ion interaction theory (SIT) approach is used to extrapolate thermodynamic constants to zero ionic strength at 25 °C.

**[2000CIA/IUL2]**

The complexation equilibria of tin(II) with differently protonated orthophosphate ions have been studied at 25 °C in 3 M NaClO<sub>4</sub> ionic medium by potentiometric titrations using both tin amalgam and glass electrodes. The concentrations of the metal and of the ligand ranged from  $2.5 \times 10^{-4}$  to  $2.5 \times 10^{-3}$  M and from 0.01 to 0.3 M, respectively. The hydrogen ion concentration varied between 0.1 and  $1.6 \times 10^{-6}$  M. The potentiometric data are consistent with the formation of the complexes: SnH<sub>2</sub>PO<sub>4</sub><sup>+</sup>, Sn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>(aq), Sn(H<sub>2</sub>PO<sub>4</sub>)(HPO<sub>4</sub>)<sup>-</sup>, SnHPO<sub>4</sub>(aq), Sn(HPO<sub>4</sub>)<sub>2</sub><sup>2-</sup>, Sn(HPO<sub>4</sub>)<sub>3</sub><sup>4-</sup> and SnPO<sub>4</sub><sup>-</sup>. The equilibrium constants determined for  $I = 3$  M were extrapolated to  $I = 0$ , using the ion interaction coefficients listed in Appendix B (Tables B-3 and B-4 ( $\alpha(\text{H}^+, \text{ClO}_4^-)$ ,  $\alpha(\text{Na}^+, \text{H}_2\text{PO}_4^-)$ ,  $\alpha(\text{Na}^+, \text{HPO}_4^{2-})$ ,  $\alpha(\text{Na}^+, \text{PO}_4^{3-})$ )), as well as estimated values ( $\alpha(\text{Sn}^{2+}, \text{ClO}_4^-) = 0.19 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{H}_3\text{PO}_4, \text{NaClO}_4) = 0.05 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{SnH}_2\text{PO}_4^+, \text{ClO}_4^-) = 0.11 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{Sn}(\text{H}_2\text{PO}_4)_2, \text{NaClO}_4) = 0.05 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{Na}^+, \text{Sn}(\text{H}_2\text{PO}_4)(\text{HPO}_4)^-) = -0.13 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{SnHPO}_4, \text{NaClO}_4) = 0.08 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{Na}^+, \text{Sn}(\text{HPO}_4)_2^{2-}) = 0.00 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{Na}^+, \text{Sn}(\text{HPO}_4)_3^{4-}) = -0.23 \text{ mol}\cdot\text{kg}^{-1}$ ,  $\alpha(\text{Na}^+, \text{SnPO}_4^-) = 0.03 \text{ mol}\cdot\text{kg}^{-1}$ ). The estimation of the ion interaction coefficients of the complex species were based on Eqs B.22 and B.23 (Appendix B). The experimental work was done carefully, but the validity of the estimated ion interaction coefficients is uncertain. Therefore the reported thermodynamic formation constants are only useful estimates.

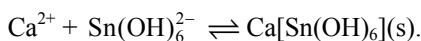
**[2000LOT/OCH]**

The solubility of Sn(IV) in cementitious systems is directly related to the presence of dissolved Ca. In the presence of typical Ca concentrations, solid Ca[Sn(OH)<sub>6</sub>](s) is



precipitated, resulting in dissolved tin(IV) concentrations that are about four to six orders of magnitude lower than observed in alkaline, Ca-free systems.

A constant  $\log_{10} K = 9.85$  at  $I = 0$  has been derived for the formation of fresh  $\text{Ca}[\text{Sn}(\text{OH})_6](\text{precip.})$  according to the reaction:



A constant of  $\log_{10} K = 10.93$  has been derived in undersaturation experiments with crystalline  $\text{Ca}[\text{Sn}(\text{OH})_6](\text{cr})$ .

The presence of Ca under alkaline conditions reduces the solubility of Sn(IV) (and Nb(V)) drastically.  $\text{Ca}[\text{Sn}(\text{OH})_6](\text{cr})$ , burtite, is an IMA-recognised mineral including Sn.

### [2000SHE/RAG]

EXAFS spectroscopic measurements were performed on 0.1 M  $\text{SnCl}_2$  and 0.01 M  $\text{SnCl}_4$  solutions in presence of chloride ion excess at temperatures from 25 °C to 350 °C. In chloride concentrations between 0.5 and 2.5 M, aqueous tin(II) forms  $\text{SnCl}_3^-$  and  $\text{SnCl}_4^{2-}$ , the latter being more stable at higher temperature (the average number of bound chloride ions increased from 3.4 (25 °C) to 3.9 (350 °C)). In solution containing 0.11 M HCl and 2.0 M NaCl, aqueous tin(IV) occurs exclusively as the  $\text{SnCl}_6^{2-}$  complex. The possible formation of mixed hydroxido-chlorido complexes of tin(IV) was not considered in this paper.

### [2001CIA]

This review paper summarises the results obtained in the author's laboratory on the complex formation equilibria of orthophosphate ions with the cations  $\text{H}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$  and  $\text{Al}^{3+}$  (at 25 °C in 3 M  $\text{NaClO}_4$ ). A variety of mixed metal-proton-phosphate species has been detected for most of the cations. Polynuclear complexes were identified only in the cases of  $\text{H}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  systems.

### [2001MUL/SEW]

The aim of this study was to gain insight into the aqueous chemistry of tin(II) at elevated temperatures and pressures. For this purpose, the UV spectra of solutions containing tin(II) ( $[\text{Sn}^{2+}]_{\text{tot}} = 1.0 \times 10^{-4} - 5.0 \times 10^{-4}$  m), 0.01 m HCl and varying concentrations of NaCl ( $[\text{NaCl}] = 0$  to 2.936 m) have been measured under argon atmosphere from 25 to 300 °C and at the equilibrium saturated vapour pressure of the system. The thermodynamic formation constants of the individual tin(II) chlorido complexes were calculated from the spectrophotometric data using an extended Debye-Hückel equation, related to that used in SIT. Between 25 and 150 °C, a scheme including five species of  $\text{SnCl}_q^{2-q}$  ( $0 \leq q \leq 4$ ) best fitted the available data. The presence of  $\text{SnCl}_4^{2-}$  was not detected above 150 °C under the conditions used. The enthalpies of

the reactions  $\text{SnCl}_q^{2-q} + \text{Cl}^- \rightleftharpoons \text{SnCl}_{q+1}^{1-q}$  ( $q = 0, 1, 2, 3$ ) were also derived from the temperature dependence of the thermodynamic formation constants. It was concluded that tin(II) chlorido complexes could be important in the transport and deposition of tin by hydrothermal ore solutions of moderate to high salinity. The extended Debye-Hückel equation used by the authors to calculate the individual ion activity coefficients is not strictly identical with that applied in the SIT, therefore an uncertainty of  $\pm 0.3$  has been assigned to the  $\log_{10} \beta_q^\circ$  values reported for 25 °C. The values of  $\ln \beta_q$  values for the stepwise formation  $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$  and  $\text{SnCl}_3^-$  as a function of temperature were fitted to the equation

$$\ln K_q = A + B(T/K) + C(T/K)^2 \quad (\text{A.87})$$

where  $T$  is in Kelvin. The values that best fit the temperature variation of each equilibrium constants are given in Table A-70.

Table A-70: Coefficients in Eq. (A.87) to define the stepwise equilibrium constants of  $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$  and  $\text{SnCl}_3^-$  with temperature up to 598.15 K.

	<i>A</i>	<i>B</i>	<i>C</i>
$\ln K_1^\circ = \ln \beta_1$	4.1523	$-5.9524 \times 10^{-3}$	$1.0187 \times 10^{-5}$
$\ln K_2^\circ$	3.7022	$-1.4290 \times 10^{-2}$	$2.6030 \times 10^{-5}$
$\ln K_3^\circ$	7.3819	$-4.1145 \times 10^{-3}$	$5.7661 \times 10^{-5}$

The equations describing the temperature variation of the stepwise equilibrium constants were differentiated to give  $\Delta_r H_m^\circ$  for the formation of  $\text{SnCl}^+$ ,  $\text{SnCl}_2(\text{aq})$  and  $\text{SnCl}_3^-$  at different temperature (see Table VIII-19).

### [2001PER/HEF]

A detailed investigation of the Pb(II)/OH<sup>-</sup> system has been made in NaClO<sub>4</sub> media at 25 °C. Combined UV-vis spectrophotometric-potentiometric titrations at  $[\text{Pb(II)}]_{\text{T}} \leq 10 \mu\text{M}$  using a long path length cell detected only four mononuclear hydroxido complexes. The values of  $\log_{10} \beta_{1q}^*$ , for the equilibria  $\text{Pb}^{2+} + q\text{H}_2\text{O(l)} \rightleftharpoons \text{Pb(OH)}_q^{2-q} + q\text{H}^+$ , were  $-7.2$ ,  $-16.1$ ,  $-26.5$ , and  $-38.0$  for  $q = 1$  to 4, respectively, at ionic strength  $I = 1 \text{ M}$  (NaClO<sub>4</sub>). Similar results were obtained at  $I = 5 \text{ M}$  (NaClO<sub>4</sub>). No evidence was found for higher order complexes ( $q > 4$ ) even at very high  $[\text{OH}^-]/[\text{Pb(II)}]$  ratios, nor for polynuclear species at  $[\text{Pb(II)}]_{\text{T}} \leq 10 \mu\text{M}$ . Measurements using 207Pb-NMR and Raman spectroscopies and differential pulse polarography (DPP) provided only semiquantitative confirmation. The mononuclear  $\text{Pb(OH)}_q^{2-q}(\text{aq})$  complexes are the only hydrolyzed species likely to be significant under typical environmental and biological conditions.

**[2001PER/KUN]**

Molar heat capacities at constant pressure of six solid solutions and 11 intermediate phases in the Pd-Pb, Pd-Sn and Pd-In systems were determined each 10 K by differential scanning calorimetry from 310 to 1000 K. The experimental values have been fitted by polynomials. Results are given, discussed and compared with available literature data.

This paper gives new  $C_{p,m}^{\circ}$  results for 17 different alloys of palladium with indium, tin or lead. The scarcity of data in literature does not allow a throughout comparison and a crosscheck of our work. Our own investigations indicate that the most probable uncertainty of our measurements is about 5% or  $1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Further investigations are necessary to extend the temperature range to higher temperatures and to improve the accuracy of the data.

These data are not useful in the present context or in any context because they do not meet the NEA requirements. The binary Pd-Sn system data was not targeted in the current work on Sn review.

**[2001SEB/POT]**

In this review the accuracy of published thermodynamic data on inorganic tin compounds was evaluated to obtain a reliable basis for modelling Sn migration in a deep repository of radioactive waste. Hydrolysis, complexation with halide ions or other inorganic compounds, and precipitation reactions of Sn(II) and Sn(IV) were studied. The Guggenheim-Scatchard Specific Interaction Theory was used to correct equilibrium constants to zero ionic strength. Tin(II) can be hydrolyzed into  $\text{SnOH}^+$ ,  $\text{Sn(OH)}_2(\text{aq})$  and  $\text{Sn(OH)}_3^-$  at low concentration. For higher tin levels, the  $\text{Sn}_2(\text{OH})_2^{2+}$  and  $\text{Sn}_3(\text{OH})_4^{2+}$  polynuclear species are predominant. Stability constants of these equilibria at the standard state were evaluated from data available in the literature and recommended values are proposed. Complexation reactions between tin(II) and halide ions are well known, but the complex species formed are only present in solutions when halide concentration is  $> 10^{-3} \text{ mol dm}^{-3}$  and at pH values  $< 4$ . In the presence of sulphides, selenides, or tellurides, the tin(II) ions form very stable solid phases. Because of the very low solubility of  $\text{SnO}_2(\text{s})$ , little information is available in the literature about Sn(IV) hydrolysis, complexation, or precipitation reactions.

**[2001SOL/VLA]**

The thermochemical cycle used for determination of enthalpy of  $\text{SnF}_2(\text{s})$  involved several reactions including the one for  $\text{SnO}(\text{s})$ , which is found to be consistent with the calorimetric data measured by Lavut *et al.* [1981LAV/TIM]. The value of the standard enthalpy of formation of  $\text{SnF}_2(\text{s})$  at 298.15 K:  $\Delta_f H_m^{\circ}(\text{SnF}_2, \text{s}, 298.15 \text{ K}) = -(695.2 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$  has been accepted. This value differs vastly from the

calculated/estimated value of  $-(677 \pm 10)$  kJ·mol<sup>-1</sup> by Gurvich *et al.* [1991GUR/VEY].

### [2002HUM/BER]

The Nagra/PSI Chemical Thermodynamic database was reviewed and updated to support performance assessments of the planned Swiss repositories for radioactive waste. The update from version 05/92 to 01/01 involved major revisions for most of the actinides and fission products. Altogether, >70% of the database contents have been revised. Data for U, Np, Pu, Am and Tc recommended by the NEA TDB project were considered in the update. Thermodynamic data for Th, Sn, Eu, Pd, Al, and solubility and metal complexation of sulfides and silicates were extensively reviewed. Data for Zr, Ni and Se were examined less rigorously as these elements were being reviewed in phase II of the NEA TDB project. The experiences from this 2 years team effort can be summarised as follows. Detailed in house reviews and critical appraisal of NEA recommendations greatly improved the chemical consistency and quality of the selected data. However, the authors could discern major gaps in the data, especially missing carbonate complexes. In some systems, *e.g.* Th(IV)-H<sub>2</sub>O and U(IV)-H<sub>2</sub>O, experimental data could not be described by a unique set of thermodynamic constants. There, a pragmatic approach based on solubility data was chosen for application to performance assessment.

### [2003CAH/DAV]

Thermodynamic and phase diagram data relative to the O-Sn system have been assessed. The existence, the type and the temperature of invariant equilibria  $\text{Melt1(l)} \rightleftharpoons \text{Melt2(l)} + \text{SnO}_2\text{(s)}$  and  $\text{Sn}_3\text{O}_4\text{(s)} \rightleftharpoons 2\text{SnO(s)} + \text{SnO}_2\text{(s)}$  have been the subject of DSC and XRD experiments. The adjustable parameters of the modelling are obtained by the CALculation of PHase Diagram (CALPHAD) method fitted thanks to diagram and thermodynamic data through Thermo-Calc<sup>TM</sup> software. In particular, the liquid phase is described by the way of Hillert's partially ionic liquid model. The final result is in good agreement with all of the experimental data available. Activities of tin and oxygen versus composition at different high temperatures can be calculated.

### [2003DUN/CRA]

Pewter plates and implements have been recovered and examined from what is believed to be the wreck site of *Queen Anne's Revenge*, flagship of the pirate Blackbeard, that sank near Beaufort, North Carolina in 1718. All of the pewter artefacts from the site display a surface veneer of corrosion products. Mineralogical examination of the pewter samples revealed that the corrosion products are composed of romarchite (SnO), hydromarchite (Sn<sub>3</sub>O<sub>2</sub>(OH)<sub>2</sub>), and abhurite (Sn<sub>21</sub>Cl<sub>16</sub>(OH)<sub>14</sub>O<sub>6</sub>).

Observation and identification of these phases will be useful in understanding the stability of tin oxides/hydroxides in the weathering environment and the nature of the metal's corrosion products.

### [2003LOR]

Basic quantities for the description of the solubility are reviewed and tabulated. It is distinguished between quantities based on mass, on the amount of substance, on the volume, and on combinations of these 3 terms. Furthermore, special quantities to describe the solubility of gases are introduced. They are related to the amount fraction, the molality, or to Henry's law constant of the dissolved gas. Approximate relations are given connecting the Ostwald, Bunsen, and Kuenen (Künen) coefficients. Finally, relations among the Sechenov parameters are presented describing salt effects on the solubility of gases.

### [2003YEN/GRO]

A thermodynamic assessment of the Hg-Sn system was carried out using the CALPHAD method. The comprehensive assessment covers the extensive phase diagram data as well as the enthalpy, activity, and vapour pressure data. Two cases of intermetallic compounds in the Hg + Sn system are considered. Case 1 considers the intermetallic compounds  $\beta$ ,  $\gamma$ , and  $\text{HgSn}_4$  as having no solubility and can thus be treated as the stoichiometric phases  $\beta\text{-HgSn}_{38}$ ,  $\gamma\text{-HgSn}_{12}$ , and  $\text{HgSn}_4$ . Case 2 uses a sublattice model to more accurately describe a solubility of the  $\gamma$  phase; it also considers the stoichiometric  $\delta\text{-HgSn}_7$  phase. The  $\varepsilon$  phase was considered to be metastable and neglected in the thermodynamic assessment. Thermodynamic parameters were optimised using all the assessed experimental thermodynamic and phase equilibrium data. Both calculated phase diagrams of the Hg-Sn system (Cases 1 and 2) and the thermodynamic data are reasonable and satisfactory when compared with literature data. Future crucial experiments are suggested.

### [2004DUN/CRA]

Corrosion products were examined from typical pewter artefacts originating from six different submerged archaeological sites, dating to between ca. A.D. 1550 and 1733, along the eastern seaboard of North America and in the Caribbean Sea. The artefacts were viewed as 270 to 450 year long experiments revealing the phases and mechanisms of tin corrosion in seawater. All of the samples analyzed exhibit abhurite ( $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ ), romarchite ( $\text{SnO}$ ), and hydroromarchite ( $\text{Sn}_6(\text{OH})_4\text{O}_4$ ) forming at the expense of the underlying artefact. Textural analysis suggests that abhurite is the first alteration product to form at the expense of the pewter; romarchite subsequently develops and then hydroromarchite. The outermost corrosion layers on several of the most corroded artefacts also exhibit cassiterite ( $\text{SnO}_2$ ) as a significant and apparently final phase to form during alteration. The absence of this mineral on many samples demonstrates that, while samples appeared to be stable under the conditions that were

present, cassiterite had not yet had time to form. The universal appearance of romarchite on corroding tin suggests that it is a required step in the oxidation of pure tin to the final most stable phase of cassiterite.

The authors state that no data are available in the literature on the (thermodynamic) stability of abhurite and hydromarchite. This is not true for abhurite whose thermodynamic stability has been determined by Edwards *et al.* [1992EDW/GIL]. Moreover the composition of abhurite has been determined to be  $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$  by its single-crystal structure [1981SCH/NES].

### [2004GUR/GAV2]

This paper has been translated from Geokhimiya, No. 10, (2004) pp. 1096-1105, [2004GUR/GAV]. Gurevich *et al.* [2004GUR/GAV2] measured the heat capacity of cassiterite in the temperature range of 13.4 to 336 K using adiabatic calorimetry and they calculated values of heat capacity, entropy and enthalpy increment which are presented in Tables A-71 and A-72.

The experimental data were approximated by a Debye-Einstein-Kieffer equation

$$C_{p,m}^{\circ}(T) = n[a_1D(\theta_1/T) + a_2D(\theta_2/T) + a_3D(\theta_3/T) + a_4E(\theta_E/T) + a_5K(\theta_L/T, \theta_U/T)] \quad (\text{A.88})$$

where  $n$  is the number of atoms in the formula ( $n = 3$ , for  $\text{SnO}_2$ ),  $D$ ,  $E$ , and  $K$  are Debye function, Einstein function and  $K$ -function of Kieffer [1979KIE]:  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ ,  $\theta_E$ ,  $\theta_L$ , and  $\theta_U$  are their characteristic temperatures;  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ , and  $a_5$  are linear coefficients. Thus eleven adjustable parameters have to be selected.  $D$ ,  $E$ , and  $K$  functions can be expressed as follows

$$D(\theta/T) \equiv 3R(\theta/T)^{-3} \int_0^{\theta/T} \xi^4 \frac{\exp(\xi)}{(\exp(\xi)-1)^2} d\xi \quad (\text{A.89})$$

$$E(\theta_E/T) \equiv 3R \frac{(\theta_E/T)^2 \exp(\theta_E/T)}{(\exp(\theta_E/T)-1)^2} \quad (\text{A.90})$$

$$K(\theta_L/T, \theta_U/T) \equiv \frac{3R}{\theta_U/T - \theta_L/T} \int_{\theta_L/T}^{\theta_U/T} \frac{\xi^2 \exp(\xi)}{(\exp(\xi)-1)^2} d\xi \quad (\text{A.91})$$

Table A-71: Experimental values of heat capacity of cassiterite SnO<sub>2</sub>(cr) for various temperatures as measured by Gurevich *et al.* [2004GUR/GAV2] and [2004GUR/GAV3].

<i>T</i> /K	$C_{p,m}^{\circ}$ (SnO <sub>2</sub> , cr)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnO <sub>2</sub> , cr)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnO <sub>2</sub> , cr)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	<i>T</i> /K	$C_{p,m}^{\circ}$ (SnO <sub>2</sub> , cr)/ J·K <sup>-1</sup> ·mol <sup>-1</sup>
RP sample: mass 3.4983 g							
52.85	6.815	108.94	22.70	178.31	38.18	261.36	51.07
56.19	7.841	112.85	23.70	183.29	39.52	271.83	52.35
59.39	8.706	116.77	24.87	188.45	40.10	277.13	52.96
62.48	9.617	120.78	25.64	193.62	41.07	282.46	53.73
65.52	10.49	124.93	26.92	198.78	41.93	287.72	54.30
68.51	11.63	129.10	27.86	204.01	42.86	292.98	54.78
71.92	12.71	133.05	28.75	209.21	43.81	298.26	55.23
75.77	13.68	137.03	29.75	214.34	44.50	299.81	55.30
79.62	14.61	141.02	30.56	219.49	45.43	305.11	55.80
83.45	15.88	145.03	31.38	224.66	46.07	310.40	56.20
86.03	16.51	149.03	32.48	229.84	46.91	315.69	56.71
89.47	17.50	153.06	33.29	235.03	47.64	320.98	57.17
93.96	18.62	157.09	34.09	240.22	48.39	326.27	57.73
97.22	19.62	165.31	35.64	245.44	49.06	331.57	58.12
101.10	20.61	169.55	36.51	250.65	49.69	336.88	58.56
105.00	21.63	173.76	37.40	255.88	50.33		
AA sample: mass 4.2955 g							
13.40	0.0726	61.19	9.317	141.56	30.76	243.50	48.86
14.50	0.0672	64.25	10.22	146.51	31.82	248.73	49.55
15.70	0.131	67.27	11.11	151.47	32.93	253.97	50.24
16.76	0.147	70.27	12.01	156.45	34.02	259.21	50.94
18.45	0.180	73.26	12.89	161.45	35.00	264.47	51.63
19.51	0.368	76.20	13.77	166.53	36.04	269.73	52.28
20.88	0.453	79.58	14.76	171.64	37.03	275.01	52.91
21.59	0.391	83.39	15.88	176.55	38.03	280.30	53.50
22.37	0.562	87.20	16.98	181.60	38.94	285.60	54.07
24.37	0.711	91.01	18.04	186.67	39.86	290.91	54.57
26.78	1.027	96.02	19.44	191.76	40.78	296.90	55.33
29.25	1.338	100.00	20.53	196.87	41.64	302.33	55.84
33.50	2.084	103.96	21.58	201.99	42.52	307.52	56.29
38.03	3.046	107.82	22.61	207.12	43.37	312.86	56.61
41.58	3.866	112.27	23.75	212.24	44.24	318.18	57.12
45.33	4.817	117.15	24.96	217.38	45.07	323.48	57.67
48.95	5.802	121.99	26.17	222.59	45.85	328.80	58.14
51.53	6.607	126.85	27.32	227.83	46.62	334.11	58.65
54.90	7.554	131.72	28.51	233.06	47.40		
58.06	8.432	136.62	29.62	238.27	48.12		

Table A-72: Thermodynamic properties of cassiterite SnO<sub>2</sub> (tetragonal) at 0 to 336 K calculated by Gurevich *et al.*<sup>1</sup> [2004GUR/GAV2] and [2004GUR/GAV3] and this review<sup>2</sup>, respectively.

<i>T</i> /K	$C_{p,m}^{\circ}(T)^{1/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$C_{p,m}^{\circ}(T)^{2/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^{1/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^{2/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{1/}$ kJ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{2/}$ kJ·mol <sup>-1</sup>
4.00	0.003	0.003	0.001	0.001	0.000	0.000
6.00	0.009	0.009	0.003	0.003	0.000	0.000
8.00	0.022	0.021	0.007	0.007	0.000	0.000
10.00	0.044	0.041	0.015	0.014	0.000	0.000
12.00	0.076	0.071	0.025	0.024	0.000	0.000
14.00	0.123	0.113	0.040	0.038	0.000	0.000
16.00	0.189	0.168	0.061	0.056	0.001	0.001
18.00	0.280	0.227	0.088	0.078	0.001	0.001
20.00	0.398	0.346	0.123	0.108	0.002	0.002
25.00	0.842	0.784	0.256	0.228	0.005	0.004
30.00	1.516	1.461	0.465	0.427	0.011	0.010
35.00	2.414	2.380	0.764	0.719	0.020	0.019
40.00	3.504	3.494	1.155	1.107	0.035	0.034
45.00	4.742	4.752	1.638	1.590	0.056	0.055
50.00	6.087	6.107	2.207	2.160	0.083	0.082
55.00	7.503	7.524	2.853	2.809	0.117	0.116
60.00	8.960	8.978	3.568	3.525	0.158	0.157
65.00	10.439	10.449	4.343	4.302	0.206	0.206
70.00	11.922	11.923	5.171	5.130	0.262	0.261
75.00	13.397	13.390	6.044	6.003	0.326	0.325
80.00	14.858	14.844	6.956	6.914	0.396	0.395
85.00	16.298	16.280	7.900	7.857	0.474	0.473
90.00	17.714	17.694	8.871	8.828	0.559	0.558
95.00	19.103	19.083	9.867	9.822	0.651	0.650
100.00	20.464	20.447	10.881	10.835	0.750	0.749
105.00	21.797	21.783	11.912	11.865	0.856	0.854
110.00	23.101	23.092	12.956	12.909	0.968	0.967
115.00	24.378	24.373	14.011	13.964	1.087	1.085
120.00	25.626	25.627	15.075	15.028	1.212	1.210
125.00	26.847	26.853	16.146	16.099	1.343	1.342
130.00	28.041	28.052	17.223	17.175	1.480	1.479
135.00	29.210	29.223	18.303	18.256	1.623	1.622
140.00	30.353	30.368	19.386	19.340	1.772	1.771
145.00	31.471	31.487	20.471	20.425	1.927	1.926
150.00	32.564	32.580	21.556	21.511	2.087	2.086

(Continued on next page)



Table A-72 (continued)

T/K	$C_{p,m}^{\circ}(T)^{1/}$	$C_{p,m}^{\circ}(T)^{2/}$	$S_m^{\circ}(T)^{1/}$	$S_m^{\circ}(T)^{2/}$	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{1/}$	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{2/}$
	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>
155.00	33.633	33.648	22.641	22.597	2.252	2.251
160.00	34.678	34.691	23.726	23.681	2.423	2.422
165.00	35.700	35.710	24.808	24.765	2.599	2.598
170.00	36.698	36.705	25.889	25.845	2.780	2.779
175.00	37.673	37.677	26.967	26.924	2.966	2.965
180.00	38.626	38.625	28.042	27.998	3.157	3.156
185.00	39.556	39.552	29.113	29.069	3.352	3.352
190.00	40.463	40.456	30.180	30.136	3.552	3.552
195.00	41.349	41.339	31.242	31.198	3.757	3.756
200.00	42.213	42.200	32.300	32.256	3.966	3.965
205.00	43.055	43.041	33.353	33.308	4.179	4.178
210.00	43.876	43.861	34.400	34.355	4.396	4.395
215.00	44.676	44.661	35.442	35.397	4.618	4.617
220.00	45.455	45.441	36.478	36.433	4.843	4.842
225.00	46.214	46.201	37.508	37.462	5.072	5.071
230.00	46.953	46.943	38.532	38.486	5.305	5.304
235.00	47.673	47.665	39.549	39.503	5.542	5.540
240.00	48.373	48.369	40.560	40.514	5.782	5.780
245.00	49.054	49.054	41.565	41.519	6.025	6.024
250.00	49.717	49.721	42.563	42.516	6.272	6.271
255.00	50.362	50.371	43.554	43.507	6.523	6.521
260.00	50.989	51.002	44.538	44.492	6.776	6.775
265.00	51.598	51.616	45.515	45.469	7.032	7.031
270.00	52.191	52.213	46.485	46.439	7.292	7.291
275.00	52.768	52.793	47.448	47.403	7.554	7.553
280.00	53.328	53.357	48.403	48.359	7.819	7.819
285.00	53.873	53.903	49.352	49.308	8.087	8.087
290.00	54.402	54.433	50.294	50.250	8.358	8.358
295.00	54.917	54.947	51.228	51.185	8.631	8.631
298.15	55.240	55.262	51.820	51.771	8.806	8.805
300.00	55.417	55.444	52.155	52.113	8.907	8.907
305.00	55.904	55.926	53.075	53.033	9.186	9.186
310.00	56.376	56.392	53.988	53.947	9.466	9.466
315.00	56.836	56.842	54.894	54.853	9.749	9.749
320.00	57.282	57.276	55.793	55.751	10.035	10.035
325.00	57.716	57.696	56.684	56.642	10.322	10.322
330.00	58.138	58.099	57.568	57.526	10.612	10.612
336.00	58.629	58.564	58.620	58.577	10.962	10.962

An attempt was made to approximate the high temperature data of Kapustinskii *et al.* [1936KAP/ZIL] as well as Gurevich *et al.*'s data [2004GUR/GAV2] in the temperature range from 296.90 to 336.88 K with Eq. (A.93). According to Kapustinskii *et al.* [1936KAP/ZIL] their  $C_{p,m}^{\circ}(T)$  function is given by the following Maier and Kelley equation [1932MAI/KEL]

$$C_{p,m}^{\circ}(T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b\cdot(T/\text{K}) + c\cdot(T/\text{K})^{-2} \quad (\text{A.92})$$

Equation (A.92) was used to calculate  $C_{p,m}^{\circ}(T)$  in the range from 595 to 1496 K.

In order to obtain a basis for the calculation of entropy and enthalpy functions at high temperature the data listed in Table A-73 were approximated by the modified Eq. (VII-21) as below, see also Figure A-49:

$$C_{p,m}^{\circ}(\text{calc}) - C_{p,m}^{\circ}(298.15 \text{ K}) = a\cdot(T - 298.15) + b\cdot(T^2 - 298.15^2) + c\cdot(T^{-2} - 298.15^{-2}) + d\cdot(T^{-3} - 298.15^{-3}) + e\cdot(T^{-0.5} - 298.15^{-0.5}) + f\cdot(T^{-1} - 298.15^{-1}). \quad (\text{A.93})$$

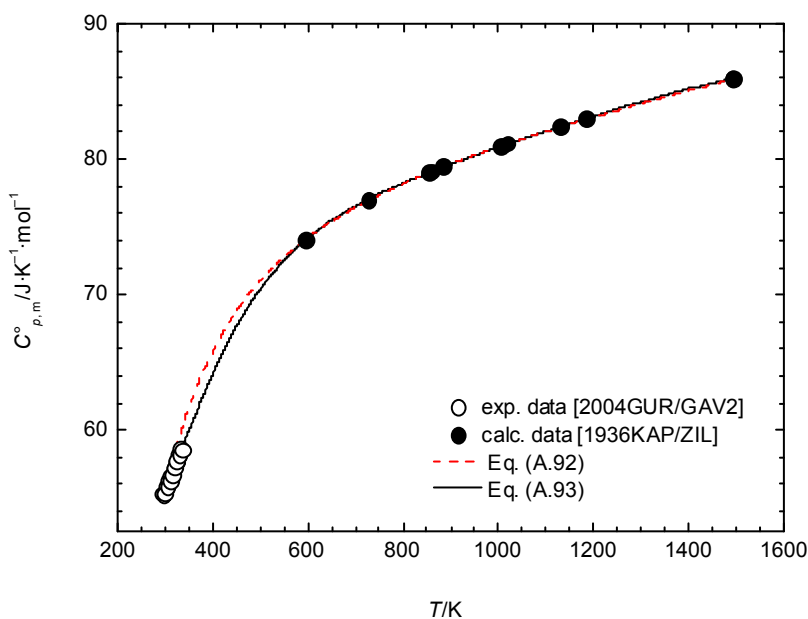
Table A-73: Heat capacity of cassiterite  $\text{SnO}_2(\text{cr})$  as measured by [2004GUR/GAV2]<sup>1</sup> and calculated according to Eq. (A.92) as recommended by [1936KAP/ZIL]<sup>2</sup>.

$T/\text{K}$	$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
296.90	55.33 <sup>1</sup>	331.57	58.12 <sup>1</sup>
302.33	55.84 <sup>1</sup>	336.88	58.56 <sup>1</sup>
307.52	56.29 <sup>1</sup>	595.15	74.0979 <sup>2</sup>
312.86	56.61 <sup>1</sup>	728.15	76.9942 <sup>2</sup>
318.18	57.12 <sup>1</sup>	855.85	79.0381 <sup>2</sup>
323.48	57.67 <sup>1</sup>	861.55	79.1191 <sup>2</sup>
328.80	58.14 <sup>1</sup>	886.45	79.4652 <sup>2</sup>
334.11	58.65 <sup>1</sup>	1006.15	80.9853 <sup>2</sup>
298.26	55.23 <sup>1</sup>	1009.15	81.0210 <sup>2</sup>
299.81	55.30 <sup>1</sup>	1020.65	81.1566 <sup>2</sup>
305.11	55.80 <sup>1</sup>	1132.15	82.4063 <sup>2</sup>
310.40	56.20 <sup>1</sup>	1187.15	82.9876 <sup>2</sup>
315.69	56.71 <sup>1</sup>	1493.15	85.9653 <sup>2</sup>
320.98	57.17 <sup>1</sup>	1495.65	85.9884 <sup>2</sup>
326.27	57.73 <sup>1</sup>		

For  $C_{p,m}^{\circ}(298.15 \text{ K})$  the value obtained from the analysis of the low temperature data was accepted. The fitting parameters of Eq. (VII.25) and Eq. (A.92) are listed below.

Table A-74: Parameters used for fitting equations (A.92), (A.93), and (VII.25).

Fitting equations	$a$	$b$	$c$	$d$	$e$	$f$
Eq. (VII.25)	$1.7419 \times 10^{-1}$	$-2.1858 \times 10^{-4}$	$-2.9144 \times 10^4$	$1.1389 \times 10^5$	$-1.0659 \times 10^3$	$4.4830 \times 10^3$
Eq. (A.93)	$2.2817 \times 10^{-1}$	$-3.8118 \times 10^{-5}$	$2.5506 \times 10^7$	$-4.9696 \times 10^8$	$3.2586 \times 10^4$	$-4.2485 \times 10^5$
Eq. (A.92)	74.785	$8.0720 \times 10^{-3}$	$-1.9450 \times 10^6$			

Figure A-49: High-temperature heat capacity of SnO<sub>2</sub>(tetr.).

The high-temperature (336 – 1500 K) values of heat capacity, entropy and enthalpy increment calculated on the basis of Eqs. (A.89), (A.90) and (A.91) are compared with the values calculated by the conventional procedure according to Eq. (A.93), see Table A-75. The data of Table A-74 could have been approximated by a simpler fitting equation, but these reviewers wanted to show that the same type of  $C_{p,m}^{\circ}(T)$  function is applicable in the low-temperature as well as in the high-temperature range.

Table A-75: Thermodynamic properties of cassiterite SnO<sub>2</sub> (tetragonal) at 336 to 1500 K calculated by Gurevich *et al.*<sup>1</sup> and this Review<sup>2</sup>, respectively.

<i>T</i> /K	$C_{p,m}^{\circ}(T)^1/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$C_{p,m}^{\circ}(T)^2/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^1/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^2/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^1/$ kJ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^2/$ kJ·mol <sup>-1</sup>
336.00	58.90	58.68	58.63	58.57	10.96	10.96
338.00	59.09	58.86	58.98	58.92	11.08	11.08
340.00	59.28	59.05	59.33	59.27	11.20	11.20
360.00	61.03	60.86	62.77	62.69	12.40	12.39
380.00	62.63	62.59	66.11	66.03	13.64	13.63
400.00	64.09	64.20	69.36	69.28	14.91	14.90
420.00	65.42	65.69	72.52	72.45	16.20	16.20
440.00	66.65	67.05	75.59	75.54	17.52	17.52
460.00	67.77	68.28	78.58	78.55	18.87	18.88
480.00	68.81	69.39	81.49	81.48	20.23	20.25
500.00	69.77	70.40	84.32	84.33	21.62	21.65
520.00	70.66	71.31	87.07	87.11	23.02	23.07
540.00	71.48	72.14	89.75	89.82	24.45	24.50
560.00	72.25	72.88	92.37	92.46	25.88	25.96
580.00	72.97	73.56	94.91	95.03	27.34	27.42
600.00	73.64	74.17	97.40	97.53	28.80	28.90
620.00	74.27	74.73	99.82	99.97	30.28	30.39
640.00	74.86	75.24	102.19	102.35	31.77	31.89
660.00	75.41	75.72	104.50	104.67	33.27	33.40
680.00	75.94	76.15	106.76	106.94	34.79	34.91
700.00	76.43	76.56	108.97	109.15	36.31	36.44
720.00	76.90	76.94	111.13	111.32	37.85	37.98
740.00	77.35	77.29	113.24	113.43	39.39	39.52
760.00	77.77	77.63	115.31	115.50	40.94	41.07
780.00	78.18	77.95	117.34	117.52	42.50	42.62
800.00	78.57	78.26	119.32	119.49	44.07	44.19
820.00	78.94	78.55	121.27	121.43	45.64	45.75
840.00	79.29	78.83	123.17	123.33	47.22	47.33
860.00	79.63	79.11	125.04	125.18	48.81	48.91
880.00	79.96	79.37	126.88	127.01	50.41	50.49
900.00	80.28	79.63	128.68	128.79	52.01	52.08
920.00	80.58	79.89	130.45	130.55	53.62	53.68
940.00	80.87	80.14	132.18	132.27	55.23	55.28
960.00	81.16	80.39	133.89	133.96	56.85	56.88
980.00	81.44	80.63	135.56	135.62	58.48	58.49
1000.00	81.70	80.88	137.21	137.25	60.11	60.11

(Continued on next page)

Table A-75 (continued)

<i>T</i> /K	$C_{p,m}^{\circ}(T)^{1/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$C_{p,m}^{\circ}(T)^{2/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^{1/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S_m^{\circ}(T)^{2/}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{1/}$ kJ·mol <sup>-1</sup>	$H^{\circ}(T) - H^{\circ}(0\text{ K})^{2/}$ kJ·mol <sup>-1</sup>
1020.00	81.96	81.12	138.83	138.85	61.75	61.73
1040.00	82.22	81.35	140.43	140.43	63.39	63.35
1060.00	82.46	81.59	141.99	141.98	65.04	64.98
1080.00	82.70	81.82	143.54	143.51	66.69	66.62
1100.00	82.94	82.05	145.06	145.01	68.34	68.26
1120.00	83.17	82.28	146.55	146.49	70.01	69.90
1140.00	83.39	82.51	148.03	147.95	71.67	71.55
1160.00	83.61	82.73	149.48	149.39	73.34	73.20
1180.00	83.82	82.96	150.91	150.80	75.02	74.86
1200.00	84.03	83.18	152.32	152.20	76.69	76.52
1220.00	84.24	83.40	153.71	153.58	78.38	78.18
1240.00	84.44	83.61	155.08	154.93	80.06	79.85
1260.00	84.64	83.82	156.44	156.27	81.75	81.53
1280.00	84.83	84.03	157.77	157.60	83.45	83.21
1300.00	85.03	84.24	159.09	158.90	85.15	84.89
1320.00	85.22	84.44	160.39	160.19	86.85	86.58
1340.00	85.40	84.63	161.67	161.46	88.56	88.27
1360.00	85.59	84.83	162.94	162.71	90.27	89.96
1380.00	85.77	85.01	164.19	163.95	91.98	91.66
1400.00	85.95	85.20	165.42	165.18	93.70	93.36
1420.00	86.12	85.37	166.64	166.39	95.42	95.07
1440.00	86.30	85.54	167.85	167.58	97.14	96.78
1460.00	86.47	85.71	169.04	168.76	98.87	98.49
1480.00	86.64	85.86	170.22	169.93	100.60	100.20
1500.00	86.81	86.01	171.38	171.09	102.34	101.92

**[2004GUR/GAV3]**

In this paper, the same experimental data have been reported as in [2004GUR/GAV2], and the heat capacity values of SnO<sub>2</sub>(cass) between 13.4 and 336.88 K were analysed by the same methods. In this paper however, the comparison of low- and high-temperature data is lacking.

**[2005GIE/POR]**

The kinetics of the disproportionation reaction of tin(II) oxide (SnO) to tin(IV) oxide (SnO<sub>2</sub>) and tin metal (Sn) was studied ex-situ and in-situ by X-ray powder diffraction with synchrotron radiation. Depending on sample preparation and decomposition temperature an intermediate oxide Sn<sub>2</sub>O<sub>3</sub> was observed. From thermal

disproportionation at different temperatures, the reaction rate law and the reaction rate coefficients  $k$  and activation energy  $E_A$  for the disproportionation of SnO and Sn<sub>2</sub>O<sub>3</sub> were extracted. The reaction follows a nucleation and growth mechanism according to Avrami-Erofeyev with a reaction exponent  $m = 2$ . At low temperatures, a synchrotron radiation-induced disproportionation of SnO was observed.

### [2008SEK/TOG]

The structures and stabilities of a series of nonstoichiometric SnO<sub>2-x</sub> compounds, which are yet unknown experimentally, are predicted using the cluster expansion technique combined with first-principles calculations. A homologous series of Sn<sub>n+1</sub>O<sub>2n</sub> in which oxygen vacancies are layered on (101) planes of the rutile lattice is discovered. The homologous crystals are composed of divalent and quadrivalent Sn atoms. No trivalent Sn atoms are formed.

### [2009GAJ/SIP]

UV spectroscopy has been applied to determine the stability of tin(IV)-chlorido complexes.

In chloride containing media the stock solution of tin(IV) ( $\approx 0.1$  M) was prepared by dissolving a known amount of SnCl<sub>4</sub>·5H<sub>2</sub>O in the given background electrolyte ( $x$  M HClO<sub>4</sub> + 1 M HCl,  $x = 3-7$ ), and its concentration was determined by ICP-AES. Sn(II) solutions ( $\approx 0.03$  M) were prepared by Tobias' method [1958TOB] using 0.03 M CuCl<sub>2</sub> dissolved in the given background electrolyte ( $x$  M HClO<sub>4</sub> + 1 M HCl,  $x = 3-7$ ). The accurate Sn(II)-concentration of the solution was determined iodometrically, immediately after preparation. The total tin content of the solutions were determined by ICP-AES, and were practically identical with the initial CuCl<sub>2</sub> concentrations, determined by complexometry.

The densities of perchloric acid solutions were taken from the literature [1989LOB]. Those of the mixed electrolytes were determined experimentally, and were found to be close to those derived from the simple mixture rule  $\Delta_{\text{mix}}V = 0$ , when aqueous solutions containing different electrolytes of the same ionic strength on *concentration basis* are mixed [1987HUM].

The stepwise formation constants of tin(IV)-chlorido complexes were determined by following the spectral changes, between 200 and 260 nm, of tin(IV) perchlorate solution upon addition of H(Cl,ClO<sub>4</sub>) solution, using a Unicam Helios  $\alpha$  spectrophotometer. The UV spectra of tin(IV) were studied as a function of the chloride concentration at five different ionic strengths, see Table A-76. The computer program PSEQUAD [1991ZEK/NAG] was used to derive the stepwise formation constants and the individual spectra of the chlorido complexes.

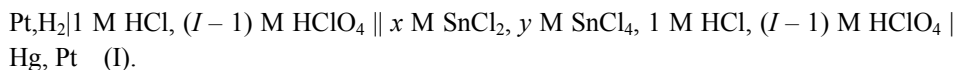
Table A-76: Experimental conditions for data sets of the UV-spectrophotometric determination of the formation constants of  $\text{SnCl}_x^{4-x}$  complexes at various ionic strengths.

$I_m (I_c)$	$[\text{Sn(IV)}]_0$	Titration solutions	$[\text{Cl}^-]$ conc. Range	No. of spectra used for the calculation
5.62 (4.5)	0.221 mM	0.02 M HCl + 4.48 M HClO <sub>4</sub> 0.2 M HCl + 4.3 M HClO <sub>4</sub> 2.0 M HCl + 2.5 HClO <sub>4</sub>	0 – 0.97 M	103
7.42 (5.6)	0.208 mM	0.02 M HCl + 5.58 M HClO <sub>4</sub> 0.2 M HCl + 5.4 M HClO <sub>4</sub> 2.0 M HCl + 3.6 HClO <sub>4</sub>	0 – 0.65 M	97
8.12 (6.0)	0.219 mM	0.02 M HCl + 5.98 M HClO <sub>4</sub> 0.2 M HCl + 5.8 M HClO <sub>4</sub> 2.0 M HCl + 4 M HClO <sub>4</sub>	0 – 0.62 M	98
10.03 (7.0)	0.220 mM	0.02 M HCl + 6.98 M HClO <sub>4</sub> 0.2 M HCl + 6.8 M HClO <sub>4</sub> 1.0 M HCl + 6.0 M HClO <sub>4</sub>	0 – 0.42 M	128
12.18 (8.0)	0.221 mM	0.02 M HCl + 7.98 M HClO <sub>4</sub> 0.2 M HCl + 7.8 M HClO <sub>4</sub> 1.0 M HCl + 7.0 M HClO <sub>4</sub>	0 – 0.32 M	88

The formation constants listed in Table A-77 have been used to extrapolate to  $I = 0$  applying the Specific Ion interaction Theory (SIT), see [1997GRE/PLY]. The resulting thermodynamic constants and the corresponding  $\Delta\epsilon$  values are also listed in Table A-77.

The ionic strength dependences of the formation constants are depicted in Figure A-50, which clearly shows that the confidence band opens up considerably at  $I = 0$ , due to long extrapolation.

For the electrochemical measurements involving chloride containing mixed background electrolyte the following electrochemical cell (I) was employed:



The cell consisted of two thermostated ( $25 \pm 0.1$ ) °C compartments ( $V_{\text{max}} = 10 \text{ cm}^3$  each), separated with a glass tube and G3 glass frit as liquid junction. For the left side, a well insulating, tightly fitted Teflon-made lid was constructed, with three inlets: one for the  $\text{H}_2/\text{Pt}$  electrode, the second for the  $\text{H}_2$ -bubbling and the third one for allowing the excess  $\text{H}_2$  to leave (which provides a permanent overpressure to avoid oxygen diffusion into the system).

Table A-77: Formation constants  $\beta_x$  of  $\text{SnCl}_x^{4-x}$  complexes (units on the molality basis) determined in  $\text{HClO}_4$  background solutions at different ionic strength (the estimated experimental errors ( $3\sigma$ ) are in parentheses) and extrapolated values to zero ionic strength and to  $I_m = 6.41 \text{ mol kg}^{-1}$  by SIT.

$I_m (I_c)$	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_4$	$\log_{10} \beta_5$	$\log_{10} \beta_6$
5.62 (4.5)	2.91(0.36)	4.96(0.36)	8.01(0.30)	8.91(0.45)	8.40(0.50)
7.42 (5.6)	2.80(0.30)	5.19(0.30)	8.75(0.30)	9.81(0.40)	9.89(0.40)
8.12 (6.0)	3.13(0.12)	5.77(0.10)	9.27(0.12)	10.20(0.15)	10.15(0.18)
10.03 (7.0)	3.52(0.15)	6.57(0.12)	10.39(0.10)	11.38(0.10)	11.69(0.12)
12.18 (8.0)	4.40(0.30)	7.45(0.15)	11.69(0.10)	12.43(0.12)	12.67(0.15)
$\rightarrow 0^\dagger$	$3.19 \pm 0.50$	$5.95 \pm 0.36$	$9.57 \pm 0.32$	$10.93 \pm 0.41$	$9.83 \pm 0.49$
$\Delta\epsilon/\text{kg}\cdot\text{mol}^{-1}$	$-0.26 \pm 0.06$	$-0.45 \pm 0.04$	$-0.64 \pm 0.03$	$-0.60 \pm 0.04$	$-0.67 \pm 0.05$
$\rightarrow 6.41^\ddagger \leftarrow$	$2.73 \pm 0.17$	$5.08 \pm 0.14$	$8.31 \pm 0.14$	$9.38 \pm 0.17$	$9.28 \pm 0.20$

<sup>†</sup> Extrapolation to zero ionic strength by weighted linear regression and error propagation assuming Gaussian probability distribution, and 95% confidence limits of parameters [2003BEV/ROB].

<sup>‡</sup> Interpolation to average ionic strength  $I_m = 6.41 \text{ mol}\cdot\text{kg}^{-1}$ .

For the right side, a Hg-pool electrode has been constructed, which is connected to the outside environment via a Pt-wire welded into the bottom of the glass wall of the compartment. This compartment also has a tightly fitted Teflon lid, with three inlets: in one, high purity (99.996%) Ar purging gas is led to the system, the other one for admitting the titrant solutions in the cell and the third one for venting. The quality of Ar was checked with bubbling the gas through alkaline pyrogallol solution; extensive bubbling, for a couple of hours, did not cause any discoloration in the solution, which proves, that  $\text{O}_2$  content of the Ar-gas can be considered as insignificant. The lack of  $\text{O}_2$  was also checked via adding  $\Gamma$  ions to the background solutions; resulting in no visually detectable  $\text{I}_2$  formation (in strongly acidic solutions  $\text{O}_2$  readily oxidises  $\Gamma$  ion). This control reaction also proved, that other oxidants (*i.e.*, traces of  $\text{ClO}_3^-$ ,  $\text{Cl}_2$ ) are absent from  $\text{HClO}_4$  and  $\text{HClO}_4$ -HCl background electrolytes as well.

Platinised Pt-electrodes were prepared according to the literature [1998SIP/HEF]. The electrode consists of high purity (99.999%) Pt-wire ( $d = 1.5 \text{ mm}$ ) and  $5 \text{ mm} \times 8 \text{ mm}$  high purity (99.999%) Pt-sheets. The platinisation was performed (after careful cleaning, as described in [1934BRO]), by using  $\text{H}_2\text{PtCl}_6$  in strongly acidic HCl ( $[\text{HCl}]_{\text{TOT}} = 0.2 \text{ M}$ ) solution. The two electrodes were connected to a high impedance multimeter via crocodile clips.

The experimentally observed potential values as a function of  $\lg([\text{Sn}(\text{IV})_{\text{free}}]/[\text{Sn}(\text{II})_{\text{free}}])$  are depicted in Figure A-51. The evaluation of  $E^\circ$  ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ) in chloride containing media requires the knowledge of the stepwise formation constants of the complexes  $\text{SnCl}_x^{2-x}$  and  $\text{SnCl}_x^{4-x}$ . For the former the values selected in this review were used, and the pertinent values for the latter are listed in Table A-78.



Figure A-50: Extrapolation to  $I = 0$  of the formation constants of  $\text{SnCl}_x^{4-x}$  complexes using SIT ( $x = 1(\text{A}), 6(\text{E})$ ).

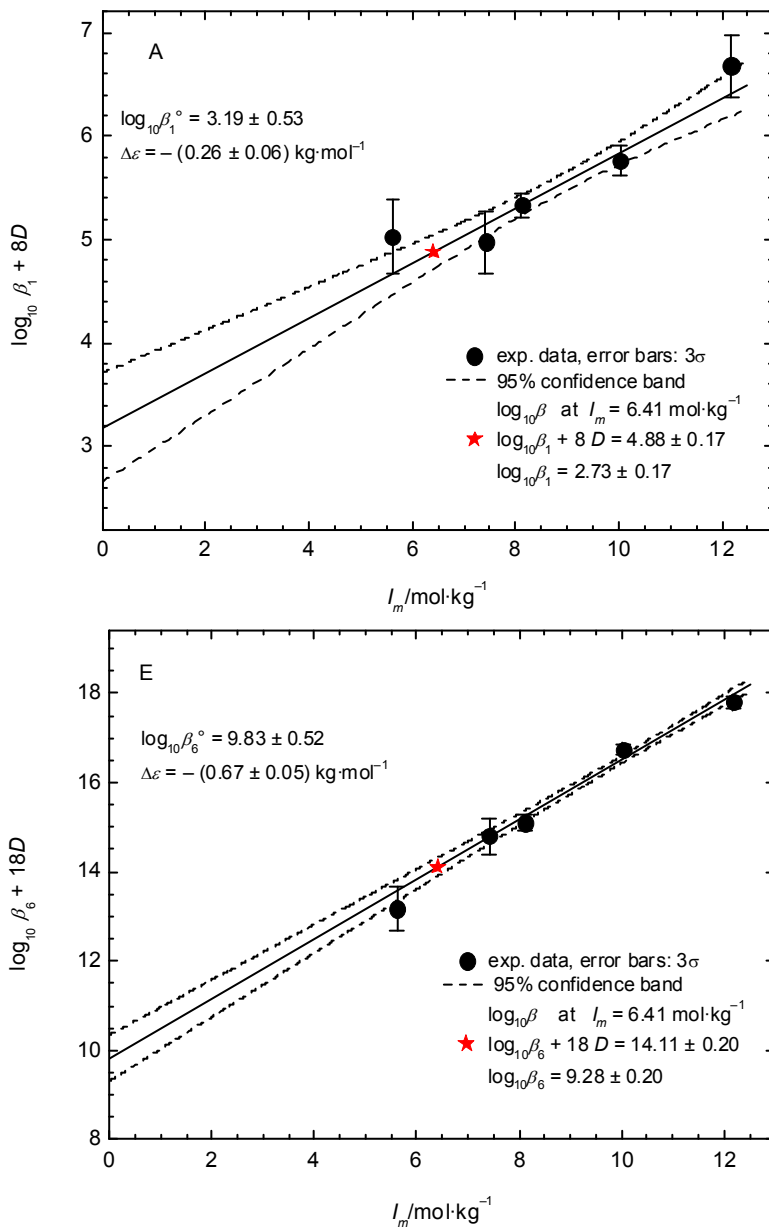
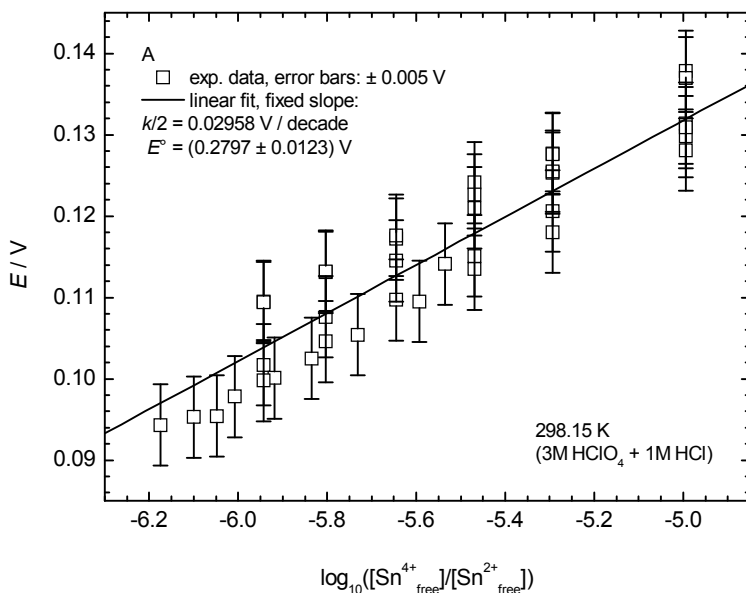


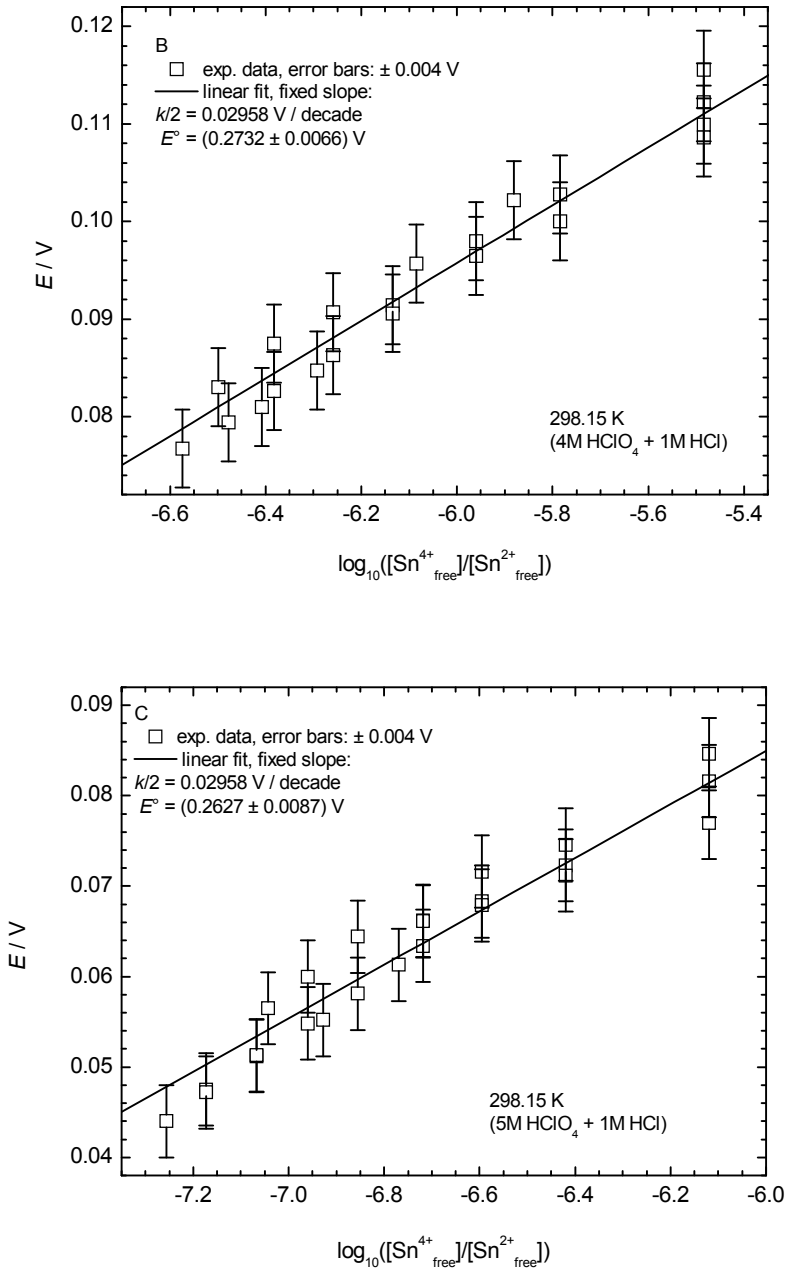
Table A-78: The formation constants used for the evaluation at different ionic strength and the calculated standard potentials.

$I_m (I_c)$	Applied formation constants (molar values) for $\text{SnCl}_n^{2-n}$	Applied formation constants (molar values) for $\text{SnCl}_n^{4-n}$	$E^\circ' (\text{Sn}^{4+}/\text{Sn}^{2+})/\text{V}$
4.73 (3 M $\text{HClO}_4$ + 1 M $\text{HCl}$ )	$\log_{10} \beta_1 = 1.26, \log_{10} \beta_2 = 1.98,$ $\log_{10} \beta_3 = 1.97, \log_{10} \beta_4 = 2.46,$	$\log_{10} \beta_1 = 2.43, \log_{10} \beta_2 = 4.59,$ $\log_{10} \beta_4 = 7.69, \log_{10} \beta_5 = 8.91,$ $\log_{10} \beta_6 = 8.74,$	$0.2797 \pm 0.0123$
6.22 (4 M $\text{HClO}_4$ + 1 M $\text{HCl}$ )	$\log_{10} \beta_1 = 1.47, \log_{10} \beta_2 = 2.36,$ $\log_{10} \beta_3 = 2.35, \log_{10} \beta_4 = 2.88,$	$\log_{10} \beta_1 = 2.78, \log_{10} \beta_2 = 5.18,$ $\log_{10} \beta_4 = 8.56, \log_{10} \beta_5 = 9.73,$ $\log_{10} \beta_6 = 9.71,$	$0.2732 \pm 0.0066$
7.88 (5 M $\text{HClO}_4$ + 1 M $\text{HCl}$ )	$\log_{10} \beta_1 = 1.74, \log_{10} \beta_2 = 2.83,$ $\log_{10} \beta_3 = 2.84, \log_{10} \beta_4 = 3.41,$	$\log_{10} \beta_1 = 3.22, \log_{10} \beta_2 = 5.94,$ $\log_{10} \beta_4 = 9.67, \log_{10} \beta_5 = 10.79,$ $\log_{10} \beta_6 = 10.94,$	$0.2627 \pm 0.0087$

Figure A-51: The observed  $E$  values of cell III as a function of  $\log_{10} ([\text{Sn}^{4+}_{\text{free}}]/[\text{Sn}^{2+}_{\text{free}}])$  at  $I_m = 4.73$  (A), 6.22 (B) and 7.88 (C) (see also Table A-78).

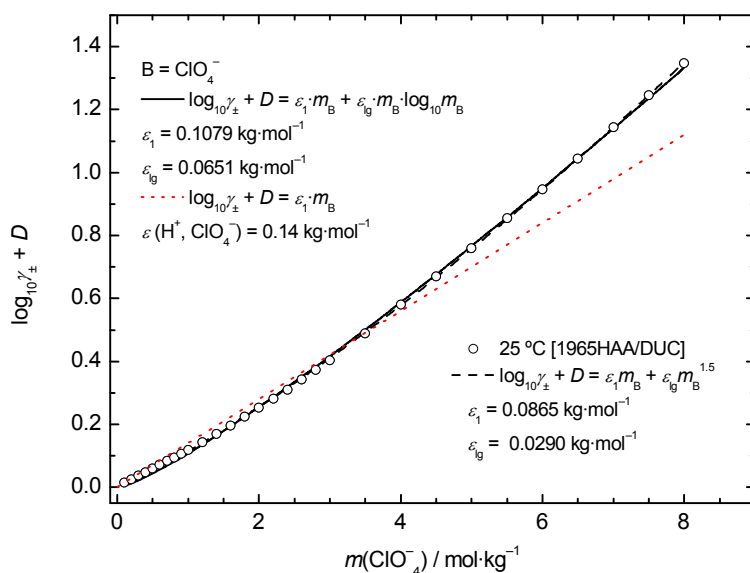
(Continued on next page)

Figure A-51 (continued)



At  $I_m > 3 \text{ mol}\cdot\text{kg}^{-1}$  the activity coefficients derived from the simple SIT equation  $\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-}$  deviate strongly from those determined experimentally, see Figure A-52. The plot  $\log_{10} \gamma_{\text{H}^+}$  vs.  $m_{\text{Cl}^-}$  looks quite similar and does not need to be shown. There are two accepted ways to extend the validity of SIT to high ionic strengths (see (i) and (ii)).

Figure A-52: Extended SIT analysis of  $\log_{10} \gamma_{\text{H}^+}$  vs.  $m_{\text{ClO}_4^-}$ .



(i) Let us assume that the analysis of  $\log_{10} \gamma_{\text{H}^+}$  vs.  $m_{\text{ClO}_4^-}$  results in

$$\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon_1(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-} + \varepsilon_{1.5}(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-}^{1.5} \quad (\text{A.94})$$

see second ionic strength expansion in unnumbered equation [1997GRE/PLY]. For the sake of brevity  $\varepsilon_1(\text{H}^+, \text{ClO}_4^-) = \varepsilon_1$  and  $\varepsilon_{1.5}(\text{H}^+, \text{ClO}_4^-) = \varepsilon_{1.5}$ .

The modified SIT approach leads to Eqs. (A.95) and (A.96) for evaluation of  $E^\ominus$  and  $\Delta\varepsilon$ .

$$E^\ominus + \frac{k}{2} [10D + 2\varepsilon_{1.5} m_{\text{ClO}_4^-}] = E^\ominus + \frac{k}{2} \Delta\varepsilon m_{\text{ClO}_4^-} \quad (\text{A.95})$$

$$E - \frac{k}{2} \left\{ \log_{10} \left[ \frac{m_{\text{Sn}^{4+}}}{m_{\text{Sn}^{2+}} m_{\text{H}^+}} \right] - 10D - 2\varepsilon_{1.5} m_{\text{ClO}_4^-}^{1.5} \right\} = E^\ominus + \frac{k}{2} \Delta\varepsilon m_{\text{ClO}_4^-} \quad (\text{A.96})$$

The values of  $\varepsilon_1 = 0.0865$  (0.10559)  $\text{kg mol}^{-1}$  and  $\varepsilon_{1.5} = 0.0290$  (0.00932)  $\text{kg}^{1.5} \cdot \text{mol}^{-1.5}$  were obtained from  $\log_{10} \gamma_{\pm}$  data at  $0.1 \leq m_{\text{ClO}_4^-} / \text{mol kg}^{-1} \leq 8.0$  [1965HAA/DUC] and  $0.001 \leq m_{\text{HCl}} / \text{mol kg}^{-1} \leq 8.0$  [1972HAM/WU], the  $\varepsilon$  values of HCl are in parenthesis.

(ii) Let us assume that the analysis of  $\log_{10} \gamma_{\text{H}^+}$  vs.  $m_{\text{ClO}_4^-}$  results in

$$\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon_1(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-} + \varepsilon_{1g}(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-} \log_{10}[m_{\text{ClO}_4^-}] \quad (\text{A.97})$$

see Table B-6.

For the sake of brevity  $\varepsilon_1(\text{H}^+, \text{ClO}_4^-) = \varepsilon_1$  and  $\varepsilon_{1g}(\text{H}^+, \text{ClO}_4^-) = \varepsilon_{1g}$ .

The modified SIT approach leads to Eqs. (A.98) and (A.99) for evaluation of  $E^\ominus$  and  $\Delta\varepsilon$ :

$$E^\ominus + \frac{k}{2} \{10D + 2\varepsilon_{1g} m_{\text{ClO}_4^-} \log_{10}[m_{\text{ClO}_4^-}]\} = E^\ominus + \frac{k}{2} \Delta\varepsilon m_{\text{ClO}_4^-} \quad (\text{A.98})$$

$$E - \frac{k}{2} \left\{ \log_{10} \left[ \frac{m_{\text{Sn}^{4+}}}{m_{\text{Sn}^{2+}} m_{\text{H}^+}^2} \right] - 10D - 2\varepsilon_{1g} m_{\text{ClO}_4^-} \log_{10}[m_{\text{ClO}_4^-}] \right\} = E^\ominus + \frac{k}{2} \Delta\varepsilon m_{\text{ClO}_4^-} \quad (\text{A.99})$$

The values of  $\varepsilon_1 = 0.1079$  (0.1121)  $\text{kg mol}^{-1}$  and  $\varepsilon_{1g} = 0.06506$  (0.02126)  $\text{kg mol}^{-1}$  were obtained from  $\log_{10} \gamma_{\pm}$  data at  $0.1 \leq m_{\text{ClO}_4^-} / \text{mol kg}^{-1} \leq 8.0$  [1965HAA/DUC] and  $0.001 \leq m_{\text{HCl}} / \text{mol kg}^{-1} \leq 8.0$  [1972HAM/WU], the  $\varepsilon$  values of HCl are in parenthesis.

As pointed out in the beginning the measurements were carried out using a mixture of HCl and HClO<sub>4</sub> as background electrolyte. Patwardhan and Kumar [1986PAT/KUM] showed that the reduced overall activity coefficient of a mixed electrolyte solution  $I^*$  is related to the reduced activity coefficients  $\Gamma_{i,r}$  of the single electrolyte solutions,  $z_i$  is the charge on single ionic species:

$$\log_{10} \Gamma_r = \log_{10} \gamma_{\pm} / (|z_+ z_-|)$$

For 1:1 electrolytes  $\Gamma_r = \gamma_{\pm}$  and  $\frac{m_i}{I}$  is the ionic strength fraction, thus

$$\log_{10} \Gamma_r^* = \sum_i \log_{10} \Gamma_{i,r} \quad (\text{A.100})$$

where the individual ionic activity coefficients  $\Gamma = \gamma_{\pm}$  have to be taken at  $m_i = I$ .

With Eq. (A.100) the modified formulae used for extrapolation read as Eqs (A.96) and (A.99), but  $\varepsilon_{1.5}$  and  $\varepsilon_{1g}$  were replaced by

$$\varepsilon_{1.5,\text{tot}} = \frac{m_{\text{HClO}_4}}{I} \varepsilon_{1.5}(\text{HClO}_4) + \frac{m_{\text{HCl}}}{I} \varepsilon_{1.5}(\text{HCl})$$

and  $\varepsilon_{1g,\text{tot}} = \frac{m_{\text{HClO}_4}}{I} \varepsilon_{1g}(\text{HClO}_4) + \frac{m_{\text{HCl}}}{I} \varepsilon_{1g}(\text{HCl})$ , respectively,

and  $m_{\text{HClO}_4}$  was replaced by  $I_m$ .

Results allowing for replacement of  $\text{HClO}_4$  by  $\text{HCl}$  are, within the experimental uncertainty, indistinguishable from those obtained by unmodified Eqs. (A.96) and (A.99). The extended SIT analysis, no matter which type is used, results in more realistic values for the ion interaction coefficient  $\alpha(\text{Sn}^{4+}, \text{ClO}_4^-)$ , 298.15 K). It was decided to calculate the standard electrode potential  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  by modified Eqs. (A.96) and (A.99). Thus the ionic medium is taken into account and these types of extended SIT analyses have been recommended by the NEA, OECD volumes on Modelling in Aquatic Chemistry [1997GRE/PLY2] and on Chemical Thermodynamics *e.g.* [2005GAM/BUG].

### [2010WHI/MOR]

The structure of an intermediate form of tin oxide was investigated by precession electron diffraction. The results support a revised version of a layered, vacancy-ordered structure for  $\text{Sn}_3\text{O}_4$  proposed in the preceding literature. The lattice parameters were found to be consistent with a monoclinic cell which is a distorted superlattice of the cassiterite structure. Zero-order Laue zone (ZOLZ) Patterson maps, phased projections and phases measured from a [001] 1<sup>st</sup>-order Laue zone (FOLZ) conditional Patterson map all support the proposed modification to the tin coordinates over the unmodified form. The results of kinematical refinement were not satisfactory, although weak features found in the Patterson maps were consistent with the O atoms being located close to the previously proposed positions.

### [2010TAN/SEK]

The cluster expansion (CE) method has been widely used as a tool to take into account the statistical thermodynamics of crystalline solutions. Here the results of a series of non-stoichiometric  $\text{SnO}_{2-x}$  compounds are presented. The calculated formation energies relative to the energies of litharge  $\text{SnO}$  and rutile  $\text{SnO}_2$  show that only  $\text{Sn}_3\text{O}_4$  and  $\text{Sn}_2\text{O}_3$  are found to be located on the convex hull of the formation energy.

## Appendix B

# Ionic strength corrections<sup>1</sup>

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [1982LAF] is adopted in this review as outlined in Section II.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which  $m_B = m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$ , and in which the activity coefficient  $\gamma_B$  is unity. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration that ensures activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state  $I = 0$ . Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [1973PIT] and in the specific ion interaction treatment.
- The other method uses an extended Debye-Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength, but it accounts for the medium specific properties by introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in

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<sup>1</sup> This appendix contains much of the text of the TDB-2 Guideline written by Grenthe and Wanner [2000GRE/WAN], earlier versions of which have been printed in the previous NEA TDB reviews. The equations presented here are an essential part of the review procedure and are required to use the selected thermodynamic values. Parts of Section B.1.1 and the contents of Tables B-4, B-5, B-6 and B-7 have been revised by Rand *et al.* [2008RAN/FUG] and in the present review.

marine chemistry, *cf.* Refs. [1979JOH/PYT], [1979MIL], [1979PYT], [1979WHI2].

The activity factor estimates are thus based on the use of Debye-Hückel type equations. The “extended” Debye-Hückel equations are either in the form of specific ion interaction methods or the Davies equation [1962DAV]. However, the Davies equation should in general not be used at ionic strengths larger than  $0.1 \text{ mol}\cdot\text{kg}^{-1}$ . The method preferred in the NEA Thermochemical Database review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction treatment in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer “B-method” [1961LEW/RAN] and the Pitzer virial coefficient method [1979PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [2000GRE/WAN].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths,  $I = 0.01$  to  $0.1 \text{ M}$ , *cf.* Figure B-1, while in other cases, notably for cations of high charge ( $\geq +4$  and  $\leq -4$ ), the lowest available ionic strength is often  $0.2 \text{ M}$  or higher, see for example Figures V.12 and V.13 in [1992GRE/FUG]. It is reasonable to assume that the extrapolated equilibrium constants at  $I = 0$  are more precise in the former than in the latter cases. The extrapolation error is composed of two parts, one due to experimental errors, and the other due to model errors. The model errors seem to be rather small for many systems, less than  $0.1$  in  $\log_{10} K^\circ$ . For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

## B.1 The specific ion interaction equations

### B.1.1 Background

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations, short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted [1922BRO], [1922BRO2] and elaborated by Scatchard [1936SCA] and Guggenheim [1966GUG]. Biedermann [1975BIE] highlighted its practical value, especially for the estimation of ionic medium effects on equilibrium constants. The two basic assumptions in the specific ion interaction treatment are described below.



• **Assumption 1:** The activity coefficient  $\gamma_j$  of an ion  $j$  of charge  $z_j$  in the solution of ionic strength  $I_m$  may be described by Eq. (B.1):

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon(j, k, I_m) m_k \quad (\text{B.1})$$

$D$  is the Debye-Hückel term:

$$D = \frac{A \sqrt{I_m}}{1 + B a_j \sqrt{I_m}} \quad (\text{B.2})$$

$A$  and  $B$  are constants which are temperature and pressure dependent,  $a_j$  is an ion size parameter (“distance of closest approach”) for the hydrated ion  $j$ , and  $I_m$  is the molal ionic strength:

$$I_m = \frac{1}{2} \sum_i m_i z_i^2$$

The Debye-Hückel limiting slope,  $A$ , has a value of  $(0.509 \pm 0.001) \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at 298.15 K and 1 bar, (*cf.* Section B.1.2). The term  $B a_j$  in the denominator of Eq. (B.2) (where  $a_j$  is an “effective” ion size parameter and  $B$  is a constant determined by the temperature and the physical properties of water) has been assigned an empirical value of  $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  (Eq. (B.2a)). The value 1.5 was proposed by Scatchard [1976SCA] to minimise the ionic strength dependence of  $\varepsilon(j, k)$  for a number of electrolytes, and it was found to be particularly appropriate between  $I_m = 0.5$  and 3.5 m. A constant value of  $B a_j$  for all species simplifies modelling of both binary and multicomponent aqueous electrolyte systems, and makes it easier to give a consistent description of mean activity coefficient both in binary and multicomponent solutions ([1959ROB/STO], pp.435-441). Thus,

$$D = \frac{A I_m^{1/2}}{1 + 1.5 I_m^{1/2}} \quad (\text{B.2a})$$

It should be mentioned that some authors have proposed different values for  $B a_j$  ranging from  $B a_j = 1.0$  [1935GUG] to  $B a_j = 1.6$  [1962VAS]. However, the parameter  $B a_j$  is empirical and as such is correlated to the value of  $\varepsilon(j, k, I_m)$ . Hence, this variety of values for  $B a_j$  does not represent an uncertainty range, but rather indicates that several different sets of  $B a_j$  and  $\varepsilon(j, k, I_m)$  may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 298.15 K listed in Table B-4, Table B-5, Table B-6 and Table B-7 have thus to be used with  $B a_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ .

The summation in Eq. (B.1) extends over all ions  $k$  present in solution. Their molality is denoted by  $m_k$ , and the specific ion interaction parameters,  $\varepsilon(j, k, I_m)$ , in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium are often very much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of  $\log_{10} \gamma_j$  for the reacting ions. This fact often makes it possible to simplify the summation  $\sum_k \varepsilon(j, k, I_m) m_k$ ,

so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included, as shown in Eqs. (B.5) to (B.9).

- **Assumption 2:** The ion interaction coefficients,  $\varepsilon(j, k, I_m)$  are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that  $\varepsilon$ , which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species, but in some cases the experimental data allow determination of interaction coefficients for uncharged species with electroneutral combinations of ions, *cf.* Table B-7.

Equation (B.1) will allow fairly accurate estimates of the activity coefficients in mixtures of electrolytes if the ion interaction coefficients are known. Ion interaction coefficients for simple ions can be obtained from tabulated data of mean activity coefficients of strong electrolytes or from the corresponding osmotic coefficients. Ion interaction coefficients for complexes can either be estimated from the charge and size of the ion or determined experimentally from the variation of the equilibrium constant with the ionic strength.

Ion interaction coefficients are not strictly constant but may vary slightly with the ionic strength. The extent of this variation depends on the charge type and is small for 1:1, 1:2 and 2:1 electrolytes for molalities less than 3.5 m. The concentration dependence of the ion interaction coefficients can thus often be neglected. This point was emphasised by Guggenheim [1966GUG], who has presented a considerable amount of experimental material supporting this approach. The concentration dependence is larger for electrolytes of higher charge. In order to reproduce accurately their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis *et al.* [1961LEW/RAN], Baes and Mesmer [1976BAE/MES], or Ciavatta [1980CIA].

For cases where the uncertainties in the epsilon values collected in Table B-4 and Table B-5 are  $\pm 0.03 \text{ kg}\cdot\text{mol}^{-1}$  or greater, Ciavatta [1980CIA] proposed the use of Eq. (B.3)

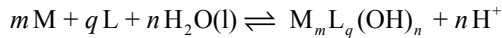
$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \quad (\text{B.3})$$

However, even if the value of  $\varepsilon$  calculated in this way describes the variation with ionic strength slightly better than a constant value, this equation has no theoretical basis;  $\varepsilon_2$  is a fitting parameter and the term  $\varepsilon_2 \log_{10} I_m$  goes to minus infinity at the limiting value  $I_m = 0$ . This expression for the composition dependence of  $\varepsilon$  should be avoided, even though the term  $\varepsilon \cdot m = (\varepsilon_1 + \varepsilon_2 \log_{10} I_m) \cdot m$  (in the calculation of activity coefficients) is zero at  $I_m = 0$ . There may be cases where reviewers will still want to use Eq. (B.3) to describe the ionic strength variation of the interaction parameters, but the rationale behind this should then be described. However, as discussed by Rand *et al.* [2008RAN/FUG] (*cf.* Section IX.1.3.3) the one- and two-epsilon models usually will

provide similar calculated results for values of  $\log_{10} K^\circ$ . As the two-epsilon model has been used in the current and previous volumes, the relevant parameters have been retained and augmented in Table B-6.

By using a more elaborate virial expansion, Pitzer and co-workers [1973PIT], [1973PIT/MAY], [1974PIT/KIM], [1974PIT/MAY], [1975PIT], [1976PIT/SIL], [1978PIT/PET], [1979PIT] have managed to describe measured activity coefficients of a large number of electrolytes with high precision over a large concentration range. Pitzer's model generally contains three parameters as compared to one in the specific ion interaction treatment. The use of the treatment requires the knowledge of all these parameters. The derivation of Pitzer coefficients for many complexes, such as those of the actinides would require a very large amount of additional experimental work, since few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction treatment is illustrated below for a general case of a complex formation reaction. Charges on all species except the hydrogen ions are omitted for brevity.



The formation constant of  $M_mL_q(OH)_n$ ,  $^*\beta_{q,n,m}$ , determined in an ionic medium (1:1 salt NX) of the ionic strength  $I_m$ , is related to the corresponding value at zero ionic strength,  $^*\beta_{q,n,m}^\circ$  by Eq. (B.4).

$$\log_{10} ^*\beta_{q,n,m} = \log_{10} ^*\beta_{q,n,m}^\circ + m \log_{10} \gamma_M + q \log_{10} \gamma_L + n \log_{10} a_{H_2O} - \log_{10} \gamma_{q,n,m} - n \log_{10} \gamma_{H^+} \quad (B.4)$$

The subscript  $(q,n,m)$  denotes the complex ion,  $M_mL_q(OH)_n$ . If the concentrations of N and X are much greater than the concentrations of M, L,  $M_mL_q(OH)_n$  and  $H^+$ , only the molalities  $m_N$  and  $m_X$  have to be taken into account for the calculation of the term,  $\sum_k \varepsilon(j,k,I_m)m_k$  in Eq. (B.1). For example, for the activity coefficient of the metal cation M,  $\gamma_M$ , Eq. (B.5) is obtained at 298.15 K and 1 bar.

$$\log_{10} \gamma_M = \frac{-z_M^2 0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \varepsilon(M,X,I_m)m_X \quad (B.5)$$

Under these conditions,  $I_m \approx m_X = m_N$ . Substituting the  $\log_{10} \gamma_j$  values in Eq. (B.4) with the corresponding forms of Eq. (B.5) and rearranging leads to:

$$\log_{10} ^*\beta_{q,n,m} - \Delta z^2 D - n \log_{10} a_{H_2O} = \log_{10} ^*\beta_{q,n,m}^\circ - \Delta \varepsilon I_m \quad (B.6)$$

where, at 298.15 K and 1 bar:

$$\Delta z^2 = (m z_M - q z_L - n)^2 + n - m z_M^2 - q z_L^2 \quad (B.7)$$

$$D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad (\text{B.8})$$

$$\Delta\varepsilon = \varepsilon(q, n, m, \text{N or X}) + n\varepsilon(\text{H}, \text{X}) - q\varepsilon(\text{N}, \text{L}) - m\varepsilon(\text{M}, \text{X}) \quad (\text{B.9})$$

Here  $(mz_M - qz_L - n)$ ,  $z_M$  and  $z_L$  are the charges of the complex,  $M_mL_q(\text{OH})_n$ , the metal ion M and the ligand L, respectively.

Equilibria involving  $\text{H}_2\text{O}(\text{l})$  as a reactant or product require a correction for the activity of water,  $a_{\text{H}_2\text{O}}$ . The activity of water in an electrolyte mixture can be calculated as:

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-\phi_m \sum_k m_k}{\ln(10)M_{\text{H}_2\text{O}}^{-1}} \quad (\text{B.10})$$

where  $\phi_m$  is the osmotic coefficient of the mixture,  $M_{\text{H}_2\text{O}}$  is the molar mass of  $\text{H}_2\text{O}$ , and the summation extends over all solute species  $k$  with molality  $m_k$  present in the solution. In the presence of an ionic medium NX as the dominant species, Eq. (B.10) can be simplified by neglecting the contributions of all minor species, *i.e.*, the reacting ions. Hence, for a 1:1 electrolyte of ionic strength  $I_m \approx m_{\text{NX}}$ , Eq. (B.10) becomes:

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-2m_{\text{NX}}\phi_m}{\ln(10)M_{\text{H}_2\text{O}}^{-1}} \quad (\text{B.11})$$

Alternatively, water activities can be taken from Table B-1. These have been calculated for the most common ionic media at various concentrations applying Pitzer's ion interaction model and the interaction parameters given in [1991PIT]. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [1959ROB/STO]. The activity of water can also be calculated from the known activity coefficients of the dissolved species. In the presence of an ionic medium,  $\text{N}_{\nu_+}\text{X}_{\nu_-}$ , of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.12) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [1961LEW/RAN]).

$$1 - \phi_m = \frac{A \ln(10) |z_+ z_-|}{I_m (B a_j)^3} \left[ 1 + B a_j \sqrt{I_m} - 2 \ln(1 + B a_j \sqrt{I_m}) - \frac{1}{1 + B a_j \sqrt{I_m}} \right] - \ln(10) \varepsilon(\text{N}, \text{X}) m_{\text{NX}} \left( \frac{\nu_+ \nu_-}{\nu_+ + \nu_-} \right) \quad (\text{B.12})$$

with the general term  $B a_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ , which is mainly used in NEA reviews (*cf.*, Section B.1.2), rather than the implied  $B a_j = 1.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  in the expressions in Lewis and Randall, and  $\nu_+$  and  $\nu_-$  are the number of cations and anions in the salt formula ( $\nu_+ z_+ = |\nu_- z_-|$ ) and in this case:

$$I_m = \frac{1}{2} |z_+ z_-| m_{\text{NX}} (v_+ + v_-).$$

Table B-1: Water activities  $a_{\text{H}_2\text{O}}$  for the most common ionic media at various concentrations applying Pitzer's ion interaction approach and the interaction parameters given in [1991PIT] and using density conversions from Table II-5. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Water activities $a_{\text{H}_2\text{O}}$ at 298.15 K								
$c$ (M)	HClO <sub>4</sub>	NaClO <sub>4</sub>	LiClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	Ba(ClO <sub>4</sub> ) <sub>2</sub>	HCl	NaCl	LiCl
0.100	0.9966	0.9966	0.9966	0.9967	0.9953	0.9966	0.9966	0.9966
0.250	0.9914	0.9917	0.9912	0.9920	0.9879	0.9914	0.9917	0.9915
0.500	0.9821	0.9833	0.9817	0.9844	0.9740	0.9823	0.9833	0.9826
0.750	0.9720	0.9747	0.9713	0.9769	0.9576	0.9726	0.9748	0.9731
1.000	0.9609	0.9660	0.9602	0.9694	0.9387	0.9620	0.9661	0.9631
1.500	0.9357	0.9476	0.9341	0.9542	0.8929	0.9386	0.9479	0.9412
2.000	0.9056	0.9279	0.9037		<i>0.8383</i>	0.9115	0.9284	0.9167
3.000	0.8285	0.8840	0.8280		<i>0.7226</i>	0.8459	0.8850	0.8589
4.000	0.7260	0.8331	<i>0.7309</i>			0.7643	0.8352	0.7991
5.000	<i>0.5982</i>	<i>0.7744</i>				0.6677	0.7782	0.7079
6.000	<i>0.4513</i>	<i>0.7075</i>				<i>0.5592</i>		<i>0.6169</i>
$c$ (M)	KCl	NH <sub>4</sub> Cl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaBr	HNO <sub>3</sub>	NaNO <sub>3</sub>	LiNO <sub>3</sub>
0.100	0.9966	0.9966	0.9953	0.9954	0.9966	0.9966	0.9967	0.9966
0.250	0.9918	0.9918	0.9880	0.9882	0.9916	0.9915	0.9919	0.9915
0.500	0.9836	0.9836	0.9744	0.9753	0.9830	0.9827	0.9841	0.9827
0.750	0.9754	0.9753	0.9585	0.9605	0.9742	0.9736	0.9764	0.9733
1.000	0.9671	0.9669	0.9399	0.9436	0.9650	0.9641	0.9688	0.9635
1.500	0.9500	0.9494	0.8939	0.9024	0.9455	0.9439	0.9536	0.9422
2.000	0.9320	0.9311	0.8358	0.8507	0.9241	0.9221	0.9385	0.9188
3.000	0.8933	0.8918	0.6866	0.7168	0.8753	0.8737	0.9079	0.8657
4.000	0.8503	0.8491	0.5083	0.5511	<i>0.8174</i>	0.8196	0.8766	0.8052
5.000		<i>0.8037</i>		<i>0.3738</i>	<i>0.7499</i>	0.7612	0.8446	0.7390
6.000					<i>0.6728</i>	<i>0.7006</i>	<i>0.8120</i>	<i>0.6696</i>
0.500	0.9843	0.9813	0.9814	0.9805	0.9789	0.9828		

(Continued on next page)

Table B-1: (continued)

Water activities $a_{\text{H}_2\text{O}}$ at 298.15 K						
$c$ (M)	$\text{NH}_4\text{NO}_3$	$\text{Na}_2\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	$\text{Na}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	$\text{NaSCN}$
0.750	0.9768	0.9732	0.9728	0.9720	0.9683	0.9736
1.000	0.9694	0.9653	0.9640	0.9637	0.9570	0.9641
1.500	0.9548	0.9491	0.9455	0.9467	0.9316	0.9438
2.000	0.9403		0.9247	0.9283	0.9014	0.9215
3.000	0.9115		0.8735		0.8235	0.8708
4.000	0.8829		0.8050		0.7195	0.8115
5.000	0.8545				0.5887	0.7436
6.000	0.8266					0.6685

The activity of water is obtained by inserting Eq. (B.12) into Eq. (B.11). It should be mentioned that in mixed electrolytes with several components at high concentrations, it might be necessary to use Pitzer's equation to calculate the activity of water. On the other hand,  $a_{\text{H}_2\text{O}}$  is nearly constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of  $\text{H}_2\text{O}(\text{l})$  can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering  $\text{NaCl}$  as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), Pitzer's equation (*cf.* [2000GRE/WAN]) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for the mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (B.1). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with,  $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$ , is necessary (*cf.* Example B.3).

### B.1.2 Ionic strength corrections at temperatures other than 25 °C (298.15 K)

Values of the Debye-Hückel parameter  $A$  in Eqs. (B.2), (B.2a) and (B.12) are listed in Table B-2 for several temperatures at a pressure of 1 bar below 100 °C and at the steam saturated pressure for  $t \geq 100$  °C. The values in Table B-2 can be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, as discussed in various references [1974HEL/KIR], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], [1990ARC/WAN], [2009PAT/HRU]. The values in Table B-2 are those from Helgeson *et al.* [1981HEL/KIR]. More recent expressions for the density and dielectric constant (*e.g.*, those of Archer and Wang [1990ARC/WAN] or Pátek *et al.* [2009PAT/HRU]) would generate very slightly different values, but the Table B-2 values should be used to provide consistent TDB activity coefficient expressions.

Table B-2: Values of the Debye-Hückel constant  $A$  as a function of temperature at a pressure of 1 bar below 100 °C and at the steam saturated pressure for  $t \geq 100$  °C. The uncertainty in the  $A$  parameter is estimated by this review to be  $\pm 0.001 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at 25 °C, and  $\pm 0.006 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at 300 °C.

$t/^\circ\text{C}$	$p/\text{bar}$	$A/\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$
0	1.00	0.491
5	1.00	0.494
10	1.00	0.498
15	1.00	0.501
20	1.00	0.505
25	1.00	0.509
30	1.00	0.514
35	1.00	0.518
40	1.00	0.523
50	1.00	0.534
75	1.00	0.564
100	1.013	0.600
125	2.32	0.642
150	4.76	0.690
175	8.92	0.745
200	15.5	0.810
250	39.7	0.979
300	85.8	1.256

In this review the term  $Ba_j$ , in the denominator of the Debye-Hückel term,  $D$  of Eq. (B.2), has been assigned a value of  $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  (Eq. (B.2a)), and is kept constant at all temperatures. Due to the variation of  $B$  with temperature, this implies a temperature dependence for ion-size parameters. Assuming the ion size is in reality constant, it becomes obvious that this simplification introduces an error in  $D$ , which increases with temperature and ionic strength. However, this error is less than  $\pm 0.01 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at  $t \leq 100 \text{ }^\circ\text{C}$  and  $I < 6 \text{ m}$ , and less than  $\pm 0.006 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at  $t \leq 50 \text{ }^\circ\text{C}$  and  $I \leq 4 \text{ m}$ .

The values of  $\varepsilon(j, k, I_m)$ , obtained with the methods described in Section B.1.3 at temperatures other than  $25 \text{ }^\circ\text{C}$ , will depend on the value adopted for  $Ba_j$ . Nevertheless, as long as a consistent approach is followed, values of  $\varepsilon(j, k, I_m)$  absorb the choice of  $Ba_j$ , and for moderate temperature intervals (between  $0$  and  $200 \text{ }^\circ\text{C}$ ) the choice  $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  is simple and is recommended by this review.

The variation of  $\varepsilon(j, k, I_m)$  with temperature is discussed by Lewis *et al.* [1961LEW/RAN], Millero [1979MIL], Helgeson *et al.* [1981HEL/KIR], [1990OEL/HEL], Giffaut *et al.* [1993GIF/VIT2] and Grenthe and Plyasunov [1997GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values of  $(\partial\varepsilon/\partial T)_p$  are usually  $\leq 0.005 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for temperatures below  $200 \text{ }^\circ\text{C}$ . Therefore, if values of  $\varepsilon(j, k, I_m)$  obtained at  $25 \text{ }^\circ\text{C}$  are used in the temperature range  $0$  to  $50 \text{ }^\circ\text{C}$  to perform ionic strength corrections, the error in  $\log_{10} \gamma_j/I_m$  will be  $\leq 0.13 \text{ kg} \cdot \text{mol}^{-1}$ . It is clear that in order to reduce the uncertainties in solubility calculations at  $t \neq 25 \text{ }^\circ\text{C}$ , studies on the variation of  $\varepsilon(j, k, I_m)$  values with temperature should be undertaken.

## B.1.3 Estimation of ion interaction coefficients

### B.1.3.1 Estimation from mean activity coefficient data

#### Example B.1:

The ion interaction coefficient  $\varepsilon(\text{H}^+, \text{Cl}^-)$  can be obtained from published values of  $\gamma_{\pm, \text{HCl}}$  versus  $m_{\text{HCl}}$ :

$$\begin{aligned} 2 \log_{10} \gamma_{\pm, \text{HCl}} &= \log_{10} \gamma_{\text{H}^+} + \log_{10} \gamma_{\text{Cl}^-} \\ &= -D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{Cl}^-} - D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{H}^+} \\ \log_{10} \gamma_{\pm, \text{HCl}} &= -D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{HCl}} \end{aligned}$$

By plotting  $(\log_{10} \gamma_{\pm, \text{HCl}} + D)$  versus  $m_{\text{HCl}}$  a straight line with the slope  $\varepsilon(\text{H}^+, \text{Cl}^-)$  is obtained. The degree of linearity should in itself indicate the range of



validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

### B.1.3.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

#### Example B.2:

Equilibrium constants are given in Table B-3 for the reaction:



The following formula is deduced from Eq. (B.6) for the extrapolation to  $I = 0$ :

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^0 - \Delta\varepsilon I_m \quad (\text{B.14})$$

Table B-3: The preparation of the experimental equilibrium constants for the extrapolation to  $I = 0$  with the specific ion interaction method at 25 °C and 1 bar, according to Reaction (B.13). The linear regression of this set of data is shown in Figure B-1.

$I_m$	$\log_{10} \beta_1$ (exp) <sup>(a)</sup>	$\log_{10} \beta_{1,m}$ <sup>(b)</sup>	$\log_{10} \beta_{1,m} + 4D$
0.10	$-0.17 \pm 0.10$	-0.174	$0.264 \pm 0.100$
0.20	$-0.25 \pm 0.10$	-0.254	$0.292 \pm 0.100$
0.26	$-0.35 \pm 0.04$	-0.357	$0.230 \pm 0.040$
0.31	$-0.39 \pm 0.04$	-0.397	$0.220 \pm 0.040$
0.41	$-0.41 \pm 0.04$	-0.420	$0.246 \pm 0.040$
0.51	$-0.32 \pm 0.10$	-0.331	$0.371 \pm 0.100$
0.57	$-0.42 \pm 0.04$	-0.432	$0.288 \pm 0.040$
0.67	$-0.34 \pm 0.04$	-0.354	$0.395 \pm 0.040$
0.89	$-0.42 \pm 0.04$	-0.438	$0.357 \pm 0.040$
1.05	$-0.31 \pm 0.10$	-0.331	$0.491 \pm 0.100$
1.05	$-0.277 \pm 0.260$	-0.298	$0.525 \pm 0.260$
1.61	$-0.24 \pm 0.10$	-0.272	$0.618 \pm 0.100$
2.21	$-0.15 \pm 0.10$	-0.193	$0.744 \pm 0.100$
2.21	$-0.12 \pm 0.10$	-0.163	$0.774 \pm 0.100$
2.82	$-0.06 \pm 0.10$	-0.112	$0.860 \pm 0.100$
3.50	$0.04 \pm 0.10$	-0.027	$0.974 \pm 0.100$

- (a) Equilibrium constants for Reaction (B.13) in aqueous NaClO<sub>4</sub> solutions, with assigned uncertainties, corrected to 25 °C where necessary. For details of the data, see Section V.4.2.1.2 of [1992GRE/FUG].
- (b) Equilibrium constants were converted from molarity to molality basis as described in Section II.2

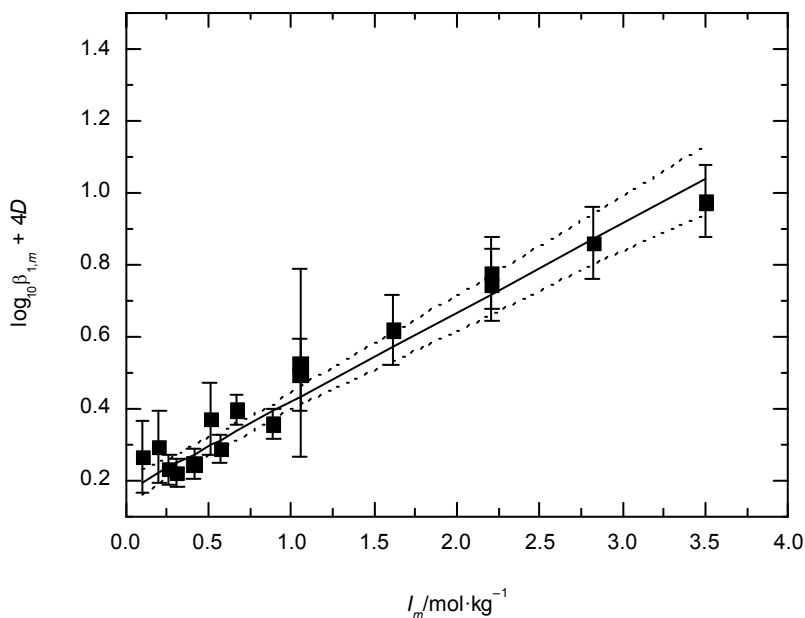
The linear regression is done as described in Appendix C. The following results are obtained:

$$\log_{10} \beta_1^\circ = (0.170 \pm 0.021)$$

$$\Delta\varepsilon(\text{B.13}) = -(0.248 \pm 0.022) \text{ kg}\cdot\text{mol}^{-1}.$$

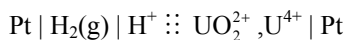
The experimental data are depicted in Figure B-1, where the area enclosed by the dotted lines represents the uncertainty range that is obtained by using the results in  $\log_{10} \beta_1^\circ$  and  $\Delta\varepsilon$  and correcting back to  $I \neq 0$ .

Figure B-1: Plot of  $\log_{10} \beta_1 + 4D$  versus  $I_m$  for Reaction (B.13), at 25 °C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at  $I = 0$  back to  $I = 4 \text{ m}$ .

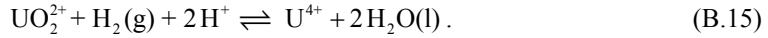


### Example B.3:

When using the specific ion interaction treatment, the relationship between the redox potential of the couple,  $\text{UO}_2^{2+}/\text{U}^{4+}$ , in a perchlorate medium of ionic strength,  $I_m$ , and the corresponding quantity at  $I = 0$  should be calculated in the following way. The reaction in the galvanic cell:



is:



For this reaction

$$\log_{10} K^\circ = \log_{10} \left( \frac{a_{\text{U}^{4+}} \cdot a_{\text{H}_2\text{O}}^2}{a_{\text{UO}_2^{2+}} \cdot a_{\text{H}^+}^2 \cdot f_{\text{H}_2}} \right).$$

$$\log_{10} K^\circ = \log_{10} K + \log_{10} \gamma_{\text{U}^{4+}} - \log_{10} \gamma_{\text{UO}_2^{2+}} - 2 \log_{10} \gamma_{\text{H}^+} - \log_{10} \gamma_{f, \text{H}_2} + 2 \log_{10} a_{\text{H}_2\text{O}},$$

$f_{\text{H}_2} \approx p_{\text{H}_2}$  at reasonably low partial pressure of  $\text{H}_2(\text{g})$ ,  $a_{\text{H}_2\text{O}} \approx 1$  (which is a reasonable approximation for  $I_m \leq 3$ ), and

$$\log_{10} \gamma_{\text{U}^{4+}} = -16D + \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

$$\log_{10} \gamma_{\text{UO}_2^{2+}} = -4D + \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

$$\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

Hence,

$$\log_{10} K^\circ = \log_{10} K - 10D + (\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-)) m_{\text{ClO}_4^-} \quad (\text{B.16})$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{RT} E \quad (\text{B.17})$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ. \quad (\text{B.18})$$

$E$  is the redox potential in a medium of ionic strength  $I$ ,  $E^\circ$  is the corresponding standard potential at  $I = 0$ , and  $n$  is the number of transferred electrons in the reaction considered. Combining Eqs. (B.16), (B.17) and (B.18) and rearranging them leads to Eq. (B.19):

$$E - 10D \left( \frac{RT \ln(10)}{nF} \right) = E^\circ - \Delta\varepsilon m_{\text{ClO}_4^-} \left( \frac{RT \ln(10)}{nF} \right) \quad (\text{B.19})$$

For  $n = 2$  in the present example and  $T = 298.15$  K, Eq. (B.19) becomes:

$$E/\text{mV} - 295.8 D = E^\circ/\text{mV} - 29.58 \Delta\varepsilon m_{\text{ClO}_4^-}$$

where

$$\Delta\varepsilon = \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-).$$

### B.1.4 On the magnitude of ion interaction coefficients

Ciavatta [1980CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complex formation reactions of various kinds were reported by Spahiu [1983SPA] and Ferri *et al.* [1983FER/GRE]. These and some other data for 25 °C and 1 bar have been collected and are listed in Section B.3.

It is obvious from the data in these tables that the charge of an ion is of great importance for determining the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al.* [1992GRE/FUG] proposed that it is possible to estimate, with an error of at most  $\pm 0.1 \text{ kg}\cdot\text{mol}^{-1}$  in  $\varepsilon$ , ion interaction coefficients for cases where there are insufficient experimental data for an extrapolation to  $I = 0$ . The error that is made by this approximation is estimated to be  $\pm 0.1 \text{ kg}\cdot\text{mol}^{-1}$  in  $\Delta\varepsilon$  in most cases, based on comparison with  $\Delta\varepsilon$  values of various reactions of the same charge type.

## B.2 Ion interaction coefficients *versus* equilibrium constants for ion pairs

It can be shown that the virial type of activity coefficient equations and the ionic pairing model are equivalent provided that the ionic pairing is weak. In these cases the distinction between complex formation and activity coefficient variations is difficult or even arbitrary unless independent experimental evidence for complex formation is available, *e.g.*, from spectroscopic data, as is the case for the weak uranium(VI) chloride complexes. It should be noted that the ion interaction coefficients evaluated and tabulated by Ciavatta [1980CIA] were obtained from experimental mean activity coefficient data without taking into account complex formation. However, it is known that many of the metal ions listed by Ciavatta form weak complexes with chloride and nitrate ion. This fact is reflected by ion interaction coefficients that are smaller than those for the non-complexing perchlorate ion, *cf.* Table B-4. This review takes chloride and nitrate complex formation into account when these ions are part of the ionic medium and uses the value of the ion interaction coefficient,  $\varepsilon(\text{M}^{n+}, \text{ClO}_4^-)$ , as a substitute for  $\varepsilon(\text{M}^{n+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{n+}, \text{NO}_3^-)$ . In this way, the medium dependence of the activity coefficients is described with a combination of a specific ion interaction model and an ion pairing model. It is evident that the use of NEA recommended data with ionic strength correction models that differ from those used in the evaluation procedure can lead to inconsistencies in the results of the speciation calculations.

It should be mentioned that complex formation may also occur between highly charged complexes and the counterion of the ionic medium. An example is the stabilisation of the complex ion,  $\text{UO}_2(\text{CO}_3)_3^{5-}$ , at high ionic strength, see for example Section V.7.1.2.1.d (p. 322) in the uranium review [1992GRE/FUG].

### B.3 Tables of ion interaction coefficients

Table B-4, Table B-5, Table B-6 and Table B-7 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction treatment described. Table B-4 contains cation interaction coefficients with  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ , Table B-5 anion interaction coefficients with  $\text{Li}^+$ ,  $\text{Na}^+$  (or  $\text{NH}_4^+$ ) and  $\text{K}^+$ , and Table B-7 neutral species – electroneutral combination of ions. The coefficients have the units of  $\text{kg}\cdot\text{mol}^{-1}$  and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in the standard order of arrangement, *cf.* Section II.1.8.

It should be noted that ion interaction coefficients tabulated in Table B-4, Table B-5 and Table B-6 may also involve ion pairing effects, as described in Section B.2. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B-4: Ion interaction coefficients  $\varepsilon(j,k)$  ( $\text{kg}\cdot\text{mol}^{-1}$ ) for cations  $j$  with  $k = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  at 298.15 K. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-6. The coefficients  $\varepsilon(\text{M}^{n+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{n+}, \text{NO}_3^-)$  reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{H}^+$	$\text{Cl}^-$	$0.12 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{ClO}_4^-$	$0.14 \pm 0.02$	
	$\text{NO}_3^-$	$0.07 \pm 0.01$	
$\text{NH}_4^+$	$\text{Cl}^-$	$-0.01 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{ClO}_4^-$	$-0.08 \pm 0.04^\dagger$	
	$\text{NO}_3^-$	$-0.06 \pm 0.03^\dagger$	
$\text{H}_2\text{gly}^+$	$\text{Cl}^-$	$-0.06 \pm 0.02$	Reported by Ciavatta [1988CIA].
	$\text{ClO}_4^-$	—	
	$\text{NO}_3^-$	—	
$\text{H}_5\text{edta}^+$	$\text{Cl}^-$	$-0.23 \pm 0.15$	See Section VIII.3.7 of [2005HUM/AND].
	$\text{ClO}_4^-$	$-0.23 \pm 0.15$	
	$\text{NO}_3^-$	$-0.23 \pm 0.15$	
$\text{SnOH}^+$	$\text{Cl}^-$	—	See Section VII.1.1 of this review.
	$\text{ClO}_4^-$	$-0.07 \pm 0.13$	
	$\text{NO}_3^-$	—	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
SnF <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.14 ± 0.10	See Section VIII.3.1.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
SnCl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.08 ± 0.07	See Section VIII.3.2.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
SnBr <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.15 ± 0.07	See Section VIII.3.3.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
SnNO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.09	See Section X.1.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
SnSCN <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.29	See Section XI.1.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
Tl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	-0.21 ± 0.06 <sup>†</sup>	
	NO <sub>3</sub> <sup>-</sup>	—	
ZnHCO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	0.2	Taken from Ferri <i>et al.</i> [1985FER/GRE].
	ClO <sub>4</sub> <sup>-</sup>	—	
	NO <sub>3</sub> <sup>-</sup>	—	
CdCl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.25 ± 0.02	Reported by Ciavatta [1980CIA].
	NO <sub>3</sub> <sup>-</sup>	—	
CdI <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
	NO <sub>3</sub> <sup>-</sup>	—	
CdSCN <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.31 ± 0.02	Reported by Ciavatta [1980CIA].
	NO <sub>3</sub> <sup>-</sup>	—	
HgCl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.19 ± 0.02	Reported by Ciavatta [1988CIA].
	NO <sub>3</sub> <sup>-</sup>	—	
Cu <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.11 ± 0.01	Reported by Ciavatta [1980CIA].
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{Ag}^+$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.00 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{NO}_3^-$	$-0.12 \pm 0.05^\dagger$	
$\text{NiOH}^+$	$\text{Cl}^-$	$-0.01 \pm 0.07$	Evaluated in [2005GAM/BUG] (Section V.3.1.1) for the reaction $\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$ from $\Delta\varepsilon$ in chloride media/perchlorate media.
	$\text{ClO}_4^-$	$0.14 \pm 0.07$	
	$\text{NO}_3^-$	—	
$\text{NiF}^+$	$\text{Cl}^-$	—	Derived from $\Delta\varepsilon = \varepsilon(\text{NiF}^+, \text{ClO}_4^-) - \varepsilon(\text{Ni}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{F}^-) = -(0.049 \pm 0.060) \text{ kg}\cdot\text{mol}^{-1}$ (see Section V.4.2.3 of [2005GAM/BUG]).
	$\text{ClO}_4^-$	$0.34 \pm 0.08$	
	$\text{NO}_3^-$	—	
$\text{NiCl}^+$	$\text{Cl}^-$	—	See details in Section V.4.2.4 of [2005GAM/BUG].
	$\text{ClO}_4^-$	$0.47 \pm 0.06$	
	$\text{NO}_3^-$	—	
$\text{NiNO}_3^+$	$\text{Cl}^-$	—	See details in Section V.6.1.2 of [2005GAM/BUG], specially sub-section V.6.1.2.1 for an alternative treatment of this system.
	$\text{ClO}_4^-$	$0.44 \pm 0.14$	
	$\text{NO}_3^-$	—	
$\text{Ni}(\text{H}_2\text{cit})^+$	$\text{Cl}^-$	—	See Section VII.7 in [2005HUM/AND].
	$\text{ClO}_4^-$	$0.12 \pm 0.50$	
	$\text{NO}_3^-$	—	
$\text{NiBr}^+$	$\text{Cl}^-$	—	See details in [2005GAM/BUG], cf. Section V.4.2.5, specially sub-section V.4.2.5.1 for an alternative treatment of this system.
	$\text{ClO}_4^-$	$0.59 \pm 0.10$	
	$\text{NO}_3^-$	—	
$\text{NiHS}^+$	$\text{Cl}^-$	—	See details in [2005GAM/BUG], Section V.5.1.1.2.
	$\text{ClO}_4^-$	$-0.85 \pm 0.39$	
	$\text{NO}_3^-$	—	
$\text{NiSCN}^+$	$\text{Cl}^-$	—	Derived from $\Delta\varepsilon = \varepsilon(\text{NiSCN}^+, \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{SCN}^-) - \varepsilon(\text{Ni}^{2+}, \text{ClO}_4^-) = -(0.109 \pm 0.025) \text{ kg}\cdot\text{mol}^{-1}$ (see [2005GAM/BUG], Section V.7.1.3.1).
	$\text{ClO}_4^-$	$0.31 \pm 0.04$	
	$\text{NO}_3^-$	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
YCO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.04	Taken from Spahiu [1983SPA].
	NO <sub>3</sub> <sup>-</sup>	—	
Am(OH) <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	-0.27 ± 0.20	Evaluated in [2003GUI/FAN] ( <i>cf.</i> Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + nH^+$ (An = Am, Cm).
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmF <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmSO <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.22 ± 0.08	Evaluated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmCO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	0.01 ± 0.05	Evaluated in [2003GUI/FAN] (Section 12.6.1.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nCO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (based on $\varepsilon(An^{3+}, Cl^-) = (0.23 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ).
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
Am(ox) <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.08 ± 0.10	See Section VI.13 of [2005HUM/AND].
	NO <sub>3</sub> <sup>-</sup>	—	
PuO <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.24 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(PuO_2^{2+}, ClO_4^-) - \varepsilon(PuO_2^+, ClO_4^-) = (0.22 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [1995CAP/VIT]. In [1992GRE/FUG], $\varepsilon(PuO_2^+, ClO_4^-) = (0.17 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ was tabulated based on [1989ROB], [1989RIG/ROB] and [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
	NO <sub>3</sub> <sup>-</sup>	—	
PuO <sub>2</sub> F <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.29 ± 0.11	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction.
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
PuO <sub>2</sub> Cl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.09	From Δε evaluated by Giffaut [1994GIF].
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	0.09 ± 0.05	See Section 12.1 of [2001LEM/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.25 ± 0.05	Derived from Δε = ε(NpO <sub>2</sub> <sup>2+</sup> , ClO <sub>4</sub> <sup>-</sup> ) - ε(NpO <sub>2</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup> ) = (0.21 ± 0.03) kg·mol <sup>-1</sup> [1987RIG/VIT], [1989RIG/ROB] and [1990RIG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> OH <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	-0.06 ± 0.40	Estimated in [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
(NpO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.45 ± 0.20	See Section 8.1.2 of [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> F <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.29 ± 0.12	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding U(IV) reaction.
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> Cl <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.14	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding Pu(VI) reaction.
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> IO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	Estimated in [2001LEM/FUG] by assuming ε(NpO <sub>2</sub> IO <sub>3</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup> ) ≈ ε(UO <sub>2</sub> IO <sub>3</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup> ).
	NO <sub>3</sub> <sup>-</sup>	—	
Np(SCN) <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.17 ± 0.04	Estimated in [2001LEM/FUG] by assuming ε(Np(SCN) <sub>3</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup> ) ≈ ε(AmF <sub>2</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup> ).
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.26 ± 0.03	Evaluated in [1992GRE/FUG], using ε(UO <sub>2</sub> <sup>2+</sup> , ClO <sub>4</sub> <sup>-</sup> ) = (0.46 ± 0.03) kg·mol <sup>-1</sup> .
	NO <sub>3</sub> <sup>-</sup>	—	

(Continued on next page)

Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
UO <sub>2</sub> OH <sup>+</sup>	Cl <sup>-</sup>	—	Evaluated in [1992GRE/FUG], using $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03)$ kg·mol <sup>-1</sup> , where X = Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> and NO <sub>3</sub> <sup>-</sup> .
	ClO <sub>4</sub> <sup>-</sup>	-0.06 ± 0.40	
	NO <sub>3</sub> <sup>-</sup>	0.51 ± 1.4	
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>	Cl <sup>-</sup>	0.81 ± 0.17	Evaluated in [1992GRE/FUG], using $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03)$ kg·mol <sup>-1</sup> , where X = Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> and NO <sub>3</sub> <sup>-</sup> .
	ClO <sub>4</sub> <sup>-</sup>	0.45 ± 0.15	
	NO <sub>3</sub> <sup>-</sup>	0.41 ± 0.22	
UF <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	0.1 ± 0.1	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.1 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> F <sup>+</sup>	Cl <sup>-</sup>	0.04 ± 0.07	Taken from Riglet <i>et al.</i> [1989RIG/ROB], where the following assumptions were made: $\varepsilon(\text{Np}^{3+}, \text{ClO}_4^-) \approx \varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) = 0.49$ kg·mol <sup>-1</sup> as for other (M <sup>3+</sup> , ClO <sub>4</sub> <sup>-</sup> ) interactions, and $\varepsilon(\text{NpO}_2^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46$ kg·mol <sup>-1</sup> .
	ClO <sub>4</sub> <sup>-</sup>	0.28 ± 0.04	See Section 9.4.2.2.1 of [2003GUI/FAN].
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> Cl <sup>+</sup>	Cl <sup>-</sup>	—	Evaluated in [1992GRE/FUG], using $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03)$ kg·mol <sup>-1</sup> , where X = Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> and NO <sub>3</sub> <sup>-</sup> .
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> ClO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> Br <sup>+</sup>	Cl <sup>-</sup>	—	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.24 ± 0.04	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> BrO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> IO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> N <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	Estimated in [1992GRE/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.3 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
UO <sub>2</sub> NO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
UO <sub>2</sub> SCN <sup>+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.22 ± 0.04	Estimated in [1992GRE/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
Th(OH) <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	0.06 ± 0.05	See Table VII-16 in Section VII.3.6.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.15 ± 0.10	
	NO <sub>3</sub> <sup>-</sup>	0.05 ± 0.15	
ThF <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.1 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	0.0 ± 0.2	
Th(NO <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	—	Evaluated in Section X.1.3.3 of [2008RAN/FUG], using $\alpha(\text{Th}^{4+}, X) = (0.70 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$ where $X = \text{ClO}_4^-$ and $\text{NO}_3^-$ .
	ClO <sub>4</sub> <sup>-</sup>	0.25 ± 0.15	
	NO <sub>3</sub> <sup>-</sup>	0.25 ± 0.15	
H <sub>6</sub> edta <sup>2+</sup>	Cl <sup>-</sup>	-0.20 ± 0.16	Evaluated in [2005HUM/AND] (Section VIII.3.7).
	ClO <sub>4</sub> <sup>-</sup>	-0.20 ± 0.16	
	NO <sub>3</sub> <sup>-</sup>	-0.20 ± 0.16	
Sn <sup>2+</sup>	Cl <sup>-</sup>	0.14 ± 0.10	See Section VI.2.1 of this review.
	ClO <sub>4</sub> <sup>-</sup>	0.19 ± 0.04	See Section VI.2.1 of this review.
	NO <sub>3</sub> <sup>-</sup>	—	
Sn <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	See Section VII.1.1 of this review.
	ClO <sub>4</sub> <sup>-</sup>	-0.02 ± 0.16	
	NO <sub>3</sub> <sup>-</sup>	—	
Pb <sup>2+</sup>	Cl <sup>-</sup>	—	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.15 ± 0.02	
	NO <sub>3</sub> <sup>-</sup>	-0.20 ± 0.12 <sup>†</sup>	
AlOH <sup>2+</sup>	Cl <sup>-</sup>	0.09	Taken from Hedlund [1988HED].
	ClO <sub>4</sub> <sup>-</sup>	0.31	
	NO <sub>3</sub> <sup>-</sup>	—	
Al <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	0.26	Taken from Hedlund [1988HED].
	ClO <sub>4</sub> <sup>-</sup>	—	
	NO <sub>3</sub> <sup>-</sup>	—	
Zn <sup>2+</sup>	Cl <sup>-</sup>	—	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.03	
	NO <sub>3</sub> <sup>-</sup>	0.16 ± 0.02	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments	
$\text{ZnCO}_3^{2+}$	$\text{Cl}^-$	$0.35 \pm 0.05$	Taken from Ferri <i>et al.</i> [1985FER/GRE].	
	$\text{ClO}_4^-$	—		
	$\text{NO}_3^-$	—		
$\text{Cd}^{2+}$	$\text{Cl}^-$	—	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	—		
	$\text{NO}_3^-$	$0.09 \pm 0.02$		
$\text{Hg}^{2+}$	$\text{Cl}^-$	—	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	$0.34 \pm 0.03$		
	$\text{NO}_3^-$	$-0.1 \pm 0.1^\dagger$		
$\text{Hg}_7^{2+}$	$\text{Cl}^-$	—	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	$0.09 \pm 0.02$		
	$\text{NO}_3^-$	$-0.2 \pm 0.1^\dagger$		
$\text{Cu}^{2+}$	$\text{Cl}^-$	$0.08 \pm 0.01$	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	$0.32 \pm 0.02$		
	$\text{NO}_3^-$	$0.11 \pm 0.01$		
$\text{Ni}^{2+}$	$\text{Cl}^-$	$0.17 \pm 0.02$	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	$0.370 \pm 0.032$		Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $\text{Ni}(\text{ClO}_4)_2$ solution ([2005GAM/BUG], Section V.4.3).
	$\text{NO}_3^-$	$0.182 \pm 0.010$		Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $\text{Ni}(\text{NO}_3)_2$ solution ([2005GAM/BUG], Section V.6.1.2.1).
$\text{Co}^{2+}$	$\text{Cl}^-$	$0.16 \pm 0.02$	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	$0.34 \pm 0.03$		
	$\text{NO}_3^-$	$0.14 \pm 0.01$		
$\text{FeOH}^{2+}$	$\text{Cl}^-$	—	Taken from Spahiu [1983SPA]	
	$\text{ClO}_4^-$	0.38		
	$\text{NO}_3^-$	—		
$\text{FeSCN}^{2+}$	$\text{Cl}^-$	—	Taken from Spahiu [1983SPA].	
	$\text{ClO}_4^-$	0.45		
	$\text{NO}_3^-$	—		
$\text{Mn}^{2+}$	$\text{Cl}^-$	$0.13 \pm 0.01$	Reported by Ciavatta [1980CIA].	
	$\text{ClO}_4^-$	—		
	$\text{NO}_3^-$	—		

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
YHCO <sub>3</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Taken from Spahiu [1983SPA].
	NO <sub>3</sub> <sup>-</sup>	—	
AmOH <sup>2+</sup>	Cl <sup>-</sup>	-0.04 ± 0.07	Evaluated in [2003GUI/FAN] ( <i>cf.</i> Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + nH^+$ .
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmF <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmCl <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmN <sub>3</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmNO <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmNO <sub>3</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmH <sub>2</sub> PO <sub>4</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
AmSCN <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO <sub>3</sub> <sup>-</sup>	—	
PuO <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+}, ClO_4^-)$ as derived from isopiestic measurements in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
PuF <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>		
	ClO <sub>4</sub> <sup>-</sup>	0.36 ± 0.17	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding U(IV) reaction.
PuCl <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	—	
	Cl <sup>-</sup>	—	
PuCl <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.16	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding Am(III) reaction.
	NO <sub>3</sub> <sup>-</sup>	—	
PuI <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(\text{PuI}^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{AmSCN}^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{NH}_4^+, \Gamma^-) \approx \varepsilon(\text{Na}^+, \text{SCN}^-)$ .
PuSCN <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	—	
	Cl <sup>-</sup>	—	
PuSCN <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(\text{PuSCN}^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{AmSCN}^{2+}, \text{ClO}_4^-)$ .
	NO <sub>3</sub> <sup>-</sup>	—	
NpO <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.46 ± 0.05	By analogy with $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$ as derived from isopiestic measurements noted in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
(NpO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	—	
	Cl <sup>-</sup>	—	
(NpO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.57 ± 0.10	See Section 8.1.2 in [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpF <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.38 ± 0.17	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding U(IV) reaction.
NpF <sub>2</sub> <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	—	
	Cl <sup>-</sup>	—	
NpSO <sub>4</sub> <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.48 ± 0.11	Estimated on Section 10.1.2.1 of [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
Np(SCN) <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.38 ± 0.20	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding U(IV) reaction.
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{UO}_2^{2+}$	$\text{Cl}^-$	$0.21 \pm 0.02$	Reported by Ciavatta [1980CIA].
	$\text{ClO}_4^-$	$0.46 \pm 0.03$	Reported by Ciavatta [1980CIA].
	$\text{NO}_3^-$	$0.24 \pm 0.03$	Reported by Ciavatta [1980CIA].
			These coefficients were not used in [1992GRE/FUG] because they were evaluated by Ciavatta [1980CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe <i>et al.</i> used $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , for $\text{X} = \text{Cl}^-$ , $\text{ClO}_4^-$ and $\text{NO}_3^-$ .
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$\text{Cl}^-$	$0.69 \pm 0.07$	Evaluated in [1992GRE/FUG], using $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , where $\text{X} = \text{Cl}^-$ , $\text{ClO}_4^-$ and $\text{NO}_3^-$ .
	$\text{ClO}_4^-$	$0.57 \pm 0.07$	
	$\text{NO}_3^-$	$0.49 \pm 0.09$	
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$\text{Cl}^-$	$0.50 \pm 0.18$	Evaluated in [1992GRE/FUG], using $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , where $\text{X} = \text{Cl}^-$ , $\text{ClO}_4^-$ and $\text{NO}_3^-$ .
	$\text{ClO}_4^-$	$0.89 \pm 0.23$	
	$\text{NO}_3^-$	$0.72 \pm 1.0$	
$\text{UF}_2^{2+}$	$\text{Cl}^-$	—	Estimated in [1992GRE/FUG].
	$\text{ClO}_4^-$	$0.3 \pm 0.1$	
	$\text{NO}_3^-$	—	
$\text{USO}_4^{2+}$	$\text{Cl}^-$	—	Estimated in [1992GRE/FUG].
	$\text{ClO}_4^-$	$0.3 \pm 0.1$	
	$\text{NO}_3^-$	—	
$\text{U}(\text{NO}_3)_2^{2+}$	$\text{Cl}^-$	—	Evaluated in [1992GRE/FUG] using $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ .
	$\text{ClO}_4^-$	$0.49 \pm 0.14$	
	$\text{NO}_3^-$	—	
$\text{Th}(\text{OH})_2^{2+}$	$\text{Cl}^-$	$0.13 \pm 0.05$	Calculated in Section VII.3.6.1 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$0.33 \pm 0.10$	
	$\text{NO}_3^-$	$0.10 \pm 0.15$	
$\text{ThF}_2^{2+}$	$\text{Cl}^-$	—	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$0.3 \pm 0.1$	
	$\text{NO}_3^-$	$0.15 \pm 0.20$	
$\text{ThSO}_4^{2+}$	$\text{Cl}^-$	$0.14 \pm 0.15$	See Section IX.1.3.2 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$0.3 \pm 0.1$	
	$\text{NO}_3^-$	—	
$\text{Th}(\text{N}_3)_2^{2+}$	$\text{Cl}^-$	—	Estimated in Section X.1.2 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$0.40 \pm 0.15$	
	$\text{NO}_3^-$	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
Th(NO <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	Estimated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(\text{Th}^{4+}, \text{X}) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ for $\text{X} = \text{ClO}_4^-$ and $\text{NO}_3^-$ .
	ClO <sub>4</sub> <sup>-</sup>	0.43 ± 0.18	
	NO <sub>3</sub> <sup>-</sup>	0.43 ± 0.18	
Th(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.4 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	—	
Th(SCN) <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	—	See Section XI.1.3.6.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.38 ± 0.20	
	NO <sub>3</sub> <sup>-</sup>	—	
Mg <sup>2+</sup>	Cl <sup>-</sup>	0.19 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.33 ± 0.03	
	NO <sub>3</sub> <sup>-</sup>	0.17 ± 0.01	
Ca <sup>2+</sup>	Cl <sup>-</sup>	0.14 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.27 ± 0.03	
	NO <sub>3</sub> <sup>-</sup>	0.02 ± 0.01	
Ba <sup>2+</sup>	Cl <sup>-</sup>	0.07 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.15 ± 0.02	
	NO <sub>3</sub> <sup>-</sup>	-0.28 ± 0.03	
Al <sup>3+</sup>	Cl <sup>-</sup>	0.33 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	—	
	NO <sub>3</sub> <sup>-</sup>	—	
Ni <sub>2</sub> OH <sup>3+</sup>	Cl <sup>-</sup>	—	By assuming $\varepsilon(\text{Ni}_2\text{OH}^{3+}, \text{ClO}_4^-) \approx \varepsilon(\text{Be}_2\text{OH}^{3+}, \text{ClO}_4^-)$ , see Section V.3.1.1 in [2005GAM/BUG].
	ClO <sub>4</sub> <sup>-</sup>	0.59 ± 0.15	
	NO <sub>3</sub> <sup>-</sup>	—	
Fe <sup>3+</sup>	Cl <sup>-</sup>	—	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.56 ± 0.03	
	NO <sub>3</sub> <sup>-</sup>	0.42 ± 0.08	
Cr <sup>3+</sup>	Cl <sup>-</sup>	0.30 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	—	
	NO <sub>3</sub> <sup>-</sup>	0.27 ± 0.02	
La <sup>3+</sup>	Cl <sup>-</sup>	0.22 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.47 ± 0.03	
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{La}^{3+} \rightarrow \text{Lu}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.47 \rightarrow 0.52$	Taken from Spahiu [1983SPA].
	$\text{NO}_3^-$	—	
$\text{Am}^{3+}$	$\text{Cl}^-$	$0.23 \pm 0.02$	The $\varepsilon(\text{An}^{3+}, \text{Cl}^-)$ for An=Am and Cm is assumed to be equal to $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-)$ which is calculated from trace activity coefficients of $\text{Nd}^{3+}$ ion in 0–4 m NaCl. These trace activity coefficients are based on the Pitzer ion interaction parameters evaluated in [1997KON/FAN] from osmotic coefficients in aqueous $\text{NdCl}_3 - \text{NaCl}$ and $\text{NdCl}_3 - \text{CaCl}_2$ .
	$\text{ClO}_4^-$	$0.49 \pm 0.03$	Estimated in [1995SIL/BID].
	$\text{NO}_3^-$	—	
$\text{Pu}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.49 \pm 0.05$	Estimated by analogy with $\varepsilon(\text{Ho}^{3+}, \text{ClO}_4^-)$ [1983SPA] as in [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	$\text{NO}_3^-$	—	
$\text{PuOH}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.50 \pm 0.05$	Estimated in [2001LEM/FUG].
	$\text{NO}_3^-$	—	
$\text{PuF}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.56 \pm 0.11$	Estimated in [2001LEM/FUG].
	$\text{NO}_3^-$	—	
$\text{PuCl}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.85 \pm 0.09$	Derived from the $\Delta\varepsilon$ evaluated in [2001LEM/FUG].
	$\text{NO}_3^-$	—	
$\text{PuBr}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.58 \pm 0.16$	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(\text{H}^+, \text{Br}^-) \approx \varepsilon(\text{Na}^+, \text{Br}^-)$ .
	$\text{NO}_3^-$	—	
$\text{Np}^{3+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.49 \pm 0.05$	Estimated by analogy with $\varepsilon(\text{Ho}^{3+}, \text{ClO}_4^-)$ [1983SPA] as in previous books in this series [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	$\text{NO}_3^-$	—	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
NpOH <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpF <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.58 ± 0.07	Evaluated in [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpCl <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.81 ± 0.09	Derived from the $\Delta\varepsilon$ selected in [2001LEM/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
NpI <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.77 ± 0.26	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(\text{H}^+, \text{I}^-) \approx \varepsilon(\text{Na}^+, \text{I}^-)$ .
	NO <sub>3</sub> <sup>-</sup>	—	
NpSCN <sup>3+</sup>	Cl <sup>-</sup>	0.76 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	ClO <sub>4</sub> <sup>-</sup>	—	
	NO <sub>3</sub> <sup>-</sup>	—	
U <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.49 ± 0.05	Evaluated in [2001LEM/FUG] by analogy with $\alpha(\text{Am}^{3+}, \text{ClO}_4^-)$ .
	NO <sub>3</sub> <sup>-</sup>	—	
UOH <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.48 ± 0.08	Evaluated in [1992GRE/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
UF <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.48 ± 0.08	Estimated in [1992GRE/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
UCI <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.10	Estimated in [2003GUI/FAN].
	NO <sub>3</sub> <sup>-</sup>	—	
UBr <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.52 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(\text{U}^{4+}, \text{X}) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ , for X = Br <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup> .
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
U <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.55 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) = (0.76 \pm 0.06)$ kg·mol <sup>-1</sup> , for X = I <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup> .
	NO <sub>3</sub> <sup>-</sup>	—	
UNO <sub>3</sub> <sup>3+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.62 ± 0.08	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) = (0.76 \pm 0.06)$ kg·mol <sup>-1</sup> for X = NO <sub>3</sub> <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup> .
	NO <sub>3</sub> <sup>-</sup>	—	
ThOH <sup>3+</sup>	Cl <sup>-</sup>	0.19 ± 0.05	See Table VII-18 in Section VII.3.6.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.48 ± 0.08	
	NO <sub>3</sub> <sup>-</sup>	0.20 ± 0.15	
ThF <sup>3+</sup>	Cl <sup>-</sup>	—	Estimated in Section VIII.1.2.1 of [2008RAN/FUG] (Table VIII-8).
	ClO <sub>4</sub> <sup>-</sup>	0.48 ± 0.08	
	NO <sub>3</sub> <sup>-</sup>	0.25 ± 0.20	
ThCl <sup>3+</sup>	Cl <sup>-</sup>	0.62 ± 0.11	Calculated in Section VIII.2.2.1.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol <sup>-1</sup> , for X = Cl <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup>
	ClO <sub>4</sub> <sup>-</sup>	0.62 ± 0.11	
	NO <sub>3</sub> <sup>-</sup>	—	
ThClO <sub>3</sub> <sup>3+</sup>	Cl <sup>-</sup>	—	Calculated in Section VIII.2.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol <sup>-1</sup> , for X = ClO <sub>3</sub> <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup>
	ClO <sub>4</sub> <sup>-</sup>	0.62 ± 0.11	
	NO <sub>3</sub> <sup>-</sup>	—	
ThBr <sup>3+</sup>	Cl <sup>-</sup>	—	Calculated in Section VIII.3.2.1 of [2008RAN/FUG] using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol <sup>-1</sup> , for X = Br <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup>
	ClO <sub>4</sub> <sup>-</sup>	0.62 ± 0.11	
	NO <sub>3</sub> <sup>-</sup>	—	
ThBrO <sub>3</sub> <sup>3+</sup>	Cl <sup>-</sup>	—	Calculated in Section VIII.3.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol <sup>-1</sup> , for X = BrO <sub>3</sub> <sup>-</sup> and ClO <sub>4</sub> <sup>-</sup>
	ClO <sub>4</sub> <sup>-</sup>	0.62 ± 0.08	
	NO <sub>3</sub> <sup>-</sup>	—	
ThN <sub>3</sub> <sup>3+</sup>	Cl <sup>-</sup>	—	See Section X.1.2 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.55 ± 0.15	
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
Th(NO <sub>3</sub> ) <sup>3+</sup>	Cl <sup>-</sup>	—	Calculated in Section X.1.3.3 of [2008RAN/FUG] using $\varepsilon(\text{Th}^{4+}, \text{X}) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ , for X = ClO <sub>4</sub> <sup>-</sup> and NO <sub>3</sub> <sup>-</sup> .
	ClO <sub>4</sub> <sup>-</sup>	0.56 ± 0.14	
	NO <sub>3</sub> <sup>-</sup>	0.56 ± 0.14	
Th(H <sub>2</sub> PO <sub>4</sub> ) <sup>3+</sup>	Cl <sup>-</sup>	—	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.5 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	—	
Th(H <sub>2</sub> PO <sub>4</sub> )(H <sub>3</sub> PO <sub>4</sub> ) <sup>3+</sup>	Cl <sup>-</sup>	—	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.5 ± 0.1	
	NO <sub>3</sub> <sup>-</sup>	—	
Th(SCN) <sup>3+</sup>	Cl <sup>-</sup>	—	See Section XI.1.3.6.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.10	
	NO <sub>3</sub> <sup>-</sup>	—	
Be <sub>2</sub> OH <sup>3+</sup>	Cl <sup>-</sup>	—	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(\text{Be}^{2+}, \text{ClO}_4^-) = 0.30 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{ClO}_4^-)$ ; $\varepsilon(\text{Be}^{2+}, \text{Cl}^-) = 0.17 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{Cl}^-)$ and $\varepsilon(\text{Be}^{2+}, \text{NO}_3^-) = 0.17 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{NO}_3^-)$ .
	ClO <sub>4</sub> <sup>-</sup>	0.50 ± 0.05	
	NO <sub>3</sub> <sup>-</sup>	—	
Be <sub>3</sub> (OH) <sub>3</sub> <sup>3+</sup>	Cl <sup>-</sup>	0.30 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(\text{Be}^{2+}, \text{ClO}_4^-) = 0.30 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{ClO}_4^-)$ ; $\varepsilon(\text{Be}^{2+}, \text{Cl}^-) = 0.17 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{Cl}^-)$ and $\varepsilon(\text{Be}^{2+}, \text{NO}_3^-) = 0.17 \text{ kg}\cdot\text{mol}^{-1}$ as for other $\varepsilon(\text{M}^{2+}, \text{NO}_3^-)$ .
	ClO <sub>4</sub> <sup>-</sup>	0.51 ± 0.05	
	NO <sub>3</sub> <sup>-</sup>	0.29 ± 0.05	
Sn <sup>4+</sup>	Cl <sup>-</sup>	—	See Section VI.3.1 of this review.
	ClO <sub>4</sub> <sup>-</sup>	0.7 ± 0.2	
	NO <sub>3</sub> <sup>-</sup>	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{Al}_3\text{HCO}_3(\text{OH})_4^{4+}$	$\text{Cl}^-$	0.41	Taken from Hedlund [1988HED].
	$\text{ClO}_4^-$	—	
	$\text{NO}_3^-$	—	
$\text{Ni}_4(\text{OH})_4^{4+}$	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$1.08 \pm 0.08$	Derived from $\Delta\varepsilon = 4\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Ni}_4\text{OH}_4^{4+}, \text{ClO}_4^-) - 4\varepsilon(\text{Ni}^{2+}, \text{ClO}_4^-)$ $= (0.16 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (see [2005GAM/BUG], Section V.3.1.1.1).
$\text{Fe}_2(\text{OH})_2^{4+}$	$\text{NO}_3^-$	—	
	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	0.82	Taken from Spahiu [1983SPA].
$\text{Y}_2\text{CO}_3^{4+}$	$\text{NO}_3^-$	—	
	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.80 \pm 0.04$	Taken from Spahiu [1983SPA].
$\text{Pu}^{4+}$	$\text{NO}_3^-$	—	
	$\text{Cl}^-$	$0.37 \pm 0.05$	Calculated in Section VI.3.1 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$0.82 \pm 0.07$	Derived from $\Delta\varepsilon = \varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) = (0.33 \pm 0.035) \text{ kg}\cdot\text{mol}^{-1}$ [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) = (1.03 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ was tabulated based on references [1989ROB], [1989RIG/ROB], [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
$\text{Np}^{4+}$	$\text{NO}_3^-$	—	
	$\text{Cl}^-$	—	
	$\text{ClO}_4^-$	$0.84 \pm 0.06$	Derived from $\Delta\varepsilon = \varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{Np}^{3+}, \text{ClO}_4^-) = (0.35 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [1989ROB], [1989RIG/ROB], [1990RIG].
	$\text{NO}_3^-$	—	

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Table B-4: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
U <sup>4+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.76 ± 0.06	Estimated in [1992GRE/FUG]. Using the measured value of $\Delta\varepsilon = \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{U}^{3+}, \text{ClO}_4^-) = (0.35 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1} \text{ p.89}$ [1990RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and $\varepsilon(\text{U}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ , a value for $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$ can be calculated in the same way as is done for $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-)$ and $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-)$ . This value, $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ is consistent with that tabulated $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ , since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$ is justified at present.
Th <sup>4+</sup>	NO <sub>3</sub> <sup>-</sup>	—	
	Cl <sup>-</sup>	0.25 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO <sub>4</sub> <sup>-</sup>	0.70 ± 0.10	Evaluated in Section VI.3.1 of [2008RAN/FUG].
Th <sub>4</sub> (OH) <sub>12</sub> <sup>4+</sup>	NO <sub>3</sub> <sup>-</sup>	0.31 ± 0.12	Evaluated in Section VI.3.1 of [2008RAN/FUG].
	Cl <sup>-</sup>	0.25 ± 0.20	See Section VII.3.4.1.3 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.56 ± 0.42	
NO <sub>3</sub> <sup>-</sup>	0.42 ± 0.50		
Th(H <sub>3</sub> PO <sub>4</sub> ) <sup>4+</sup>	Cl <sup>-</sup>	—	
	ClO <sub>4</sub> <sup>-</sup>	0.7 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO <sub>3</sub> <sup>-</sup>	—	
Al <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	Cl <sup>-</sup>	0.66	Taken from Hedlund [1988HED]
	ClO <sub>4</sub> <sup>-</sup>	1.30	Taken from Hedlund [1988HED]
	NO <sub>3</sub> <sup>-</sup>	—	
Th <sub>2</sub> (OH) <sub>3</sub> <sup>5+</sup>	Cl <sup>-</sup>	0.29 ± 0.09	Calculated in Section VII.3.4.1.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	0.91 ± 0.21	
	NO <sub>3</sub> <sup>-</sup>	0.69 ± 0.25	
Th <sub>2</sub> (OH) <sub>2</sub> <sup>6+</sup>	Cl <sup>-</sup>	0.40 ± 0.16	Evaluated in Section VII.3.4.1.1 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	1.22 ± 0.24	
	NO <sub>3</sub> <sup>-</sup>	0.69 ± 0.26	
Th <sub>4</sub> (OH) <sub>8</sub> <sup>8+</sup>	Cl <sup>-</sup>	0.70 ± 0.20	Evaluated in Section VII.3.4.1.3 of [2008RAN/FUG].
	ClO <sub>4</sub> <sup>-</sup>	1.69 ± 0.42	
	NO <sub>3</sub> <sup>-</sup>	1.59 ± 0.51	

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Table B-4: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$\text{Th}_6(\text{OH})_{15}^{9+}$	$\text{Cl}^-$	$0.72 \pm 0.30$	See details in Section VII.3.4.1.4 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$1.85 \pm 0.74$	
	$\text{NO}_3^-$	$2.20 \pm 0.77$	
$\text{Th}_6(\text{OH})_{14}^{10+}$	$\text{Cl}^-$	$0.83 \pm 0.30$	Estimated in Section VII.3.4.1.4 of [2008RAN/FUG].
	$\text{ClO}_4^-$	$2.2 \pm 0.3$	
	$\text{NO}_3^-$	$2.9 \pm 0.5$	

Table B-5: Ion interaction coefficients,  $\alpha(j,k)$  ( $\text{kg}\cdot\text{mol}^{-1}$ ), for anions  $j$  with  $k = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  at 298.15 K. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-6.

$j$	$k$	$\alpha(j,k)$	Comments
$\text{OH}^-$	$\text{Li}^+$	$-0.02 \pm 0.03^\dagger$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$0.04 \pm 0.01$	
	$\text{K}^+$	$0.09 \pm 0.01$	
$\text{F}^-$	$\text{Li}^+$	—	Evaluated in [1992GRE/FUG]. [1988CIA]
	$\text{Na}^+$	$0.02 \pm 0.02$	
	$\text{K}^+$	$0.03 \pm 0.02$	
$\text{HF}_2^-$	$\text{Li}^+$	—	Evaluated in [1992GRE/FUG].
	$\text{Na}^+$	$-0.11 \pm 0.06$	
	$\text{K}^+$	—	
$\text{Cl}^-$	$\text{Li}^+$	$0.10 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$0.03 \pm 0.01$	
	$\text{K}^+$	$0.00 \pm 0.01$	
$\text{ClO}_3^-$	$\text{Li}^+$	—	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$-0.01 \pm 0.02$	
	$\text{K}^+$	—	
$\text{ClO}_4^-$	$\text{Li}^+$	$0.15 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$0.01 \pm 0.01$	
	$\text{K}^+$	—	
$\text{Br}^-$	$\text{Li}^+$	$0.13 \pm 0.02$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$0.05 \pm 0.01$	
	$\text{K}^+$	$0.01 \pm 0.02$	
$\text{BrO}_3^-$	$\text{Li}^+$	—	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$-0.06 \pm 0.02$	
	$\text{K}^+$	—	
$\text{I}^-$	$\text{Li}^+$	$0.16 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$0.08 \pm 0.02$	
	$\text{K}^+$	$0.02 \pm 0.01$	
$\text{IO}_3^-$	$\text{Li}^+$	—	Estimated in [1992GRE/FUG].
	$\text{Na}^+$	$-0.06 \pm 0.02$	
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$\text{HSO}_4^-$	$\text{Li}^+$	— <sup>1</sup>	
	$\text{Na}^+$	$-0.01 \pm 0.02$ <sup>1</sup>	Reported by Ciavatta [1980CIA].
	$\text{K}^+$	— <sup>1</sup>	
$\text{N}_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.015 \pm 0.020$	See Section X.1.2 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{NO}_2^-$	$\text{Li}^+$	$0.06 \pm 0.04^\dagger$	
	$\text{Na}^+$	$0.00 \pm 0.02$	Reported by Ciavatta [1980CIA].
	$\text{K}^+$	$-0.04 \pm 0.02$	Reported by Ciavatta [1988CIA].
$\text{NO}_3^-$	$\text{Li}^+$	$0.08 \pm 0.01$	Reported by Ciavatta [1980CIA].
	$\text{Na}^+$	$-0.04 \pm 0.03^\dagger$	
	$\text{K}^+$	$-0.11 \pm 0.04^\dagger$	
$\text{H}_2\text{PO}_4^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.08 \pm 0.04^\dagger$	
	$\text{K}^+$	$-0.14 \pm 0.04^\dagger$	
$\text{HCO}_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.00 \pm 0.02$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	$-0.06 \pm 0.05$	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
$\text{Hox}^-$	$\text{Li}^+$	$-0.28 \pm 0.09$	Evaluated in Section VI.3.5 of [2005HUM/AND].
	$\text{Na}^+$	$-0.07 \pm 0.01$	
	$\text{K}^+$	$-0.01 \pm 0.08$	
$\text{H}_2\text{cit}^-$	$\text{Li}^+$	$-0.11 \pm 0.03$	Evaluated in Section VII.3.6 of [2005HUM/AND].
	$\text{Na}^+$	$-0.05 \pm 0.01$	
	$\text{K}^+$	$-0.04 \pm 0.01$	
$\text{CN}^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.07 \pm 0.03$	As reported in [1992BAN/BLI].
	$\text{K}^+$	—	

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<sup>1</sup> No value is tabulated here for  $\alpha(\text{H}^+, \text{HSO}_4^-)$ ; possible values are discussed in the footnote to the Appendix A entry for [1955LIS/RIV2].

Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
SCN <sup>-</sup>	Li <sup>+</sup>	—	Reported by Ciavatta [1980CIA].
	Na <sup>+</sup>	0.05 ± 0.01	
	K <sup>+</sup>	-0.01 ± 0.01	
HCOO <sup>-</sup>	Li <sup>+</sup>	—	Reported by Ciavatta [1980CIA].
	Na <sup>+</sup>	0.03 ± 0.01	
	K <sup>+</sup>	—	
CH <sub>3</sub> COO <sup>-</sup>	Li <sup>+</sup>	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	Na <sup>+</sup>	0.08 ± 0.01	
	K <sup>+</sup>	0.09 ± 0.01	
H <sub>3</sub> edta <sup>-</sup>	Li <sup>+</sup>	—	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	Na <sup>+</sup>	-0.33 ± 0.14	
	K <sup>+</sup>	-0.14 ± 0.17	
SiO(OH) <sub>3</sub> <sup>-</sup>	Li <sup>+</sup>	—	Evaluated in [1992GRE/FUG].
	Na <sup>+</sup>	-0.08 ± 0.03	
	K <sup>+</sup>	—	
Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>-</sup>	Li <sup>+</sup>	—	Estimated in [1992GRE/FUG].
	Na <sup>+</sup>	-0.08 ± 0.04	
	K <sup>+</sup>	—	
Sn(OH) <sub>3</sub> <sup>-</sup>	Li <sup>+</sup>	—	See Section VII.1.1 of this review.
	Na <sup>+</sup>	0.22 ± 0.03	
	K <sup>+</sup>	—	
SnCl <sub>3</sub> <sup>-</sup>	Li <sup>+</sup>	—	See Section VIII.3.2.1 of this review.
	Na <sup>+</sup>	0.04 ± 0.07	
	K <sup>+</sup>	—	
SnBr <sub>3</sub> <sup>-</sup>	Li <sup>+</sup>	—	See Section VIII.3.3.1 of this review.
	Na <sup>+</sup>	0.16 ± 0.08	
	K <sup>+</sup>	—	
B(OH) <sub>4</sub> <sup>-</sup>	Li <sup>+</sup>	—	
	Na <sup>+</sup>	-0.07 ± 0.05†	
	K <sup>+</sup>	—	
Ni(SCN) <sub>3</sub> <sup>-</sup>	Li <sup>+</sup>	—	Evaluated in [2005GAM/BUG] (see Section V.7.1.3.1).
	Na <sup>+</sup>	0.66 ± 0.13	
	K <sup>+</sup>	—	
Ni(cit) <sup>-</sup>	Li <sup>+</sup>	—	Evaluated in Section VII.7 of [2005HUM/AND].
	Na <sup>+</sup>	0.22 ± 0.50	
	K <sup>+</sup>	—	

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Table B-5: (continued)

$j$	$k$	$\epsilon(j,k)$	Comments
$\text{Am}(\text{SO}_4)_2^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.05 \pm 0.05$	Estimated in [1995SIL/BID].
	$\text{K}^+$	—	
$\text{Am}(\text{CO}_3)_2^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.14 \pm 0.06$	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\epsilon_n$ in NaCl solution for the reactions $\text{An}^{3+} + n\text{CO}_3^{2-} \rightleftharpoons \text{An}(\text{CO}_3)_n^{(3-2n)}$ ( $\text{An} = \text{Am}, \text{Cm}$ ) based on $\epsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02)\text{kg}\cdot\text{mol}^{-1}$ and $\epsilon(\text{Na}^+, \text{CO}_3^{2-}) = -(0.08 \pm 0.03)\text{kg}\cdot\text{mol}^{-1}$ .
	$\text{K}^+$	—	
$\text{Am}(\text{ox})_2^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.21 \pm 0.08$	Evaluated in Section VI.13 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{Am}(\text{edta})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.01 \pm 0.16$	Evaluated in Section VIII.13.2.1 of [2005HUM/AND].
	$\text{K}^+$	$0.01 \pm 0.16$	Estimated in [2005HUM/AND] Section VIII.13.2.1 by assuming $\epsilon(\text{K}^+, \text{Am}(\text{edta})^-) \approx \epsilon(\text{Na}^+, \text{Am}(\text{edta})^-)$ .
$\text{PuO}_2\text{CO}_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.18 \pm 0.18$	Estimated in [2001LEM/FUG] by analogy with $\epsilon(\text{Na}^+, \text{NpO}_2\text{CO}_3^-)$ .
	$\text{K}^+$	—	
$\text{Pu}(\text{edta})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	—	
	$\text{K}^+$	$0.01 \pm 0.16$	Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\epsilon(\text{K}^+, \text{Pu}(\text{edta})^-) \approx \epsilon(\text{Na}^+, \text{Am}(\text{edta})^-)$ .
$\text{NpO}_2(\text{OH})_2^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.01 \pm 0.07$	Estimated in [2001LEM/FUG] (Section 8.1.3).
	$\text{K}^+$	—	
$\text{NpO}_2\text{CO}_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.18 \pm 0.15$	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	$\text{K}^+$	—	
$\text{NpO}_2(\text{ox})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.4 \pm 0.1$	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$\text{NpO}_2(\text{H}_2\text{edta})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.18 \pm 0.16$	Evaluated in Section VIII.11.2.3 of [2005HUM/AND].
	$\text{K}^+$	—	
$(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.00 \pm 0.05$	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\text{K}^+$	—	
$\text{UO}_2(\text{OH})_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.09 \pm 0.05$	Estimated in [1992GRE/FUG].
	$\text{K}^+$	—	
$\text{UO}_2\text{F}_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.14 \pm 0.05$	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	$\text{K}^+$	—	
$\text{UO}_2(\text{N}_3)_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.0 \pm 0.1$	Estimated in [1992GRE/FUG].
	$\text{K}^+$	—	
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.00 \pm 0.05$	Estimated in [1992GRE/FUG].
	$\text{K}^+$	—	
$\text{UO}_2\text{cit}^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.11 \pm 0.09$	Evaluated in [2005HUM/AND].
	$\text{K}^+$	—	
$\text{Th}(\text{OH})_3(\text{CO}_3)^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.05 \pm 0.20$	See Section XI.1.3.2 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{Mg}(\text{cit})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.03 \pm 0.03$	Evaluated in [2005HUM/AND].
	$\text{K}^+$	—	
$\text{UO}_2(\text{Hedta})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.18 \pm 0.16$	Evaluated in Section VIII.10.2.4 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{Mg}(\text{Hedta})^-$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.11 \pm 0.20$	Estimated in Section VIII.5.1 of [2005HUM/AND]
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\epsilon(j,k)$	Comments
$\text{SO}_3^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.08 \pm 0.05^\dagger$	
	$\text{K}^+$	—	
$\text{SO}_4^{2-}$	$\text{Li}^+$	$-0.03 \pm 0.04^\dagger$	
	$\text{Na}^+$	$-0.12 \pm 0.06^\dagger$	
	$\text{K}^+$	$-0.06 \pm 0.02$	Reported by Ciavatta [1988CIA].
$\text{S}_2\text{O}_3^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.08 \pm 0.05^\dagger$	
	$\text{K}^+$	—	
$\text{HPO}_4^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.15 \pm 0.06^\dagger$	
	$\text{K}^+$	$-0.10 \pm 0.06^\dagger$	
$\text{CO}_3^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.08 \pm 0.03$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	$0.02 \pm 0.01$	Reported by Ciavatta [1980CIA].
$\text{ox}^{2-}$	$\text{Li}^+$	$-0.51 \pm 0.09$	Evaluated in Section VI.3.5 of [2005HUM/AND].
	$\text{Na}^+$	$-0.08 \pm 0.01$	
	$\text{K}^+$	$0.07 \pm 0.08$	
$\text{Hcit}^{2-}$	$\text{Li}^+$	$-0.17 \pm 0.04$	Evaluated in Section VII.3.6 of [2005HUM/AND].
	$\text{Na}^+$	$-0.04 \pm 0.02$	
	$\text{K}^+$	$-0.01 \pm 0.02$	
$\text{H}_2\text{edta}^{2-}$	$\text{Li}^+$	—	Evaluated in Section VII.3.7 of [2005HUM/AND].
	$\text{Na}^+$	$-0.37 \pm 0.14$	
	$\text{K}^+$	$-0.17 \pm 0.18$	
$\text{SiO}_2(\text{OH})_2^{2-}$	$\text{Li}^+$	—	Evaluated in [1992GRE/FUG].
	$\text{Na}^+$	$-0.10 \pm 0.07$	
	$\text{K}^+$	—	
$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$	$\text{Li}^+$	—	Estimated in [1992GRE/FUG].
	$\text{Na}^+$	$-0.15 \pm 0.06$	
	$\text{K}^+$	—	
$\text{Ni}(\text{ox})_2^{2-}$	$\text{Li}^+$	—	Evaluated in Section VI.7.2 of [2005HUM/AND].
	$\text{Na}^+$	$-0.26 \pm 0.03$	
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{Ni}(\text{CN})_4^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.185 \pm 0.081$	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	$\text{K}^+$	—	
$\text{CrO}_4^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.06 \pm 0.04^\dagger$	
	$\text{K}^+$	$-0.08 \pm 0.04^\dagger$	
$\text{NpO}_2(\text{HPO}_4)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.1 \pm 0.1$	Estimated in [2001LEM/FUG].
	$\text{K}^+$	—	
$\text{NpO}_2(\text{CO}_3)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.02 \pm 0.14$	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\text{K}^+$	—	
$\text{NpO}_2 \text{cit}^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.06 \pm 0.03$	Evaluated in Section VII.11 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{NpO}_2(\text{Hedta})^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.07 \pm 0.16$	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{UO}_2\text{F}_4^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.30 \pm 0.06$	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	$\text{K}^+$	—	
$\text{UO}_2(\text{SO}_4)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.12 \pm 0.06$	Estimated in [1992GRE/FUG].
	$\text{K}^+$	—	
$\text{UO}_2(\text{N}_3)_4^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.1 \pm 0.1$	Estimated in [1992GRE/FUG].
	$\text{K}^+$	—	
$\text{UO}_2(\text{ox})_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.18 \pm 0.07$	Estimated in Section VI.1.2.4.1 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{UO}_2 \text{edta}^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.22 \pm 0.18$	Estimated in Section VIII.10.2.4 of [2005HUM/AND].
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\varepsilon(j,k)$	Comments
$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.02 \pm 0.09$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	—	
$(\text{UO}_2)_2(\text{OH})_2(\text{SO}_4)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.14 \pm 0.22$	Evaluated in Section 9.5.1.1.2 of [2003GUI/FAN].
	$\text{K}^+$	—	
$\text{ThF}_6^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.30 \pm 0.06$	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{Th}(\text{SO}_4)_3^{2-}$	$\text{Li}^+$	$-0.068 \pm 0.003$	In combination with $\varepsilon_2 = (0.093 \pm 0.007)$ . See Section IX.1.3.2 of [2008RAN/FUG].
	$\text{Na}^+$	$-0.091 \pm 0.038$	
	$\text{K}^+$	$-0.091 \pm 0.038$	
$\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.1 \pm 0.2$	See Section XI.1.3.2 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.1 \pm 0.2$	See Section XI.1.3.2 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{Mg}(\text{ox})_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.15 \pm 0.03$	Estimated in Section VI.5.1 of [2005HUM/AND].
	$\text{K}^+$	$-0.15 \pm 0.10$	Estimated in [2005HUM/AND], Section VI.5.1 by assuming $\varepsilon(\text{K}^+, \text{Mg}(\text{ox})_2^{2-}) \approx \varepsilon(\text{Na}^+, \text{Mg}(\text{ox})_2^{2-})$ .
$\text{Mg}(\text{edta})^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.01 \pm 0.15$	Evaluated in Section VIII.5.2 of [2005HUM/AND].
	$\text{K}^+$	—	
$\text{Ca}(\text{ox})_2^{2-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.15 \pm 0.10$	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(\text{Na}^+, \text{Ca}(\text{ox})_2^{2-}) \approx \varepsilon(\text{Na}^+, \text{Mg}(\text{ox})_2^{2-})$ .
	$\text{K}^+$	$-0.15 \pm 0.10$	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(\text{K}^+, \text{Ca}(\text{ox})_2^{2-}) \approx \varepsilon(\text{Na}^+, \text{Mg}(\text{ox})_2^{2-})$ .
$\text{cit}^{3-}$	$\text{Li}^+$	$-0.44 \pm 0.15^\dagger$	
	$\text{Na}^+$	$-0.076 \pm 0.030^\dagger$	
	$\text{K}^+$	$0.02 \pm 0.02$	Evaluated in Section VI.3.6 of [2005HUM/AND].

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Table B-5: (continued)

<i>j</i>	<i>k</i>	$\alpha(j,k)$	Comments
Hedta <sup>3-</sup>	Li <sup>+</sup>	—	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	Na <sup>+</sup>	-0.10 ± 0.14	
	K <sup>+</sup>	0.31 ± 0.18	
PO <sub>4</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Reported by Ciavatta [1980CIA].
	Na <sup>+</sup>	-0.25 ± 0.03†	
	K <sup>+</sup>	-0.09 ± 0.02	
Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Estimated in [1992GRE/FUG].
	Na <sup>+</sup>	-0.25 ± 0.03	
	K <sup>+</sup>	—	
Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Estimated in [1992GRE/FUG].
	Na <sup>+</sup>	-0.25 ± 0.03	
	K <sup>+</sup>	—	
Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Estimated in [1992GRE/FUG].
	Na <sup>+</sup>	-0.25 ± 0.03	
	K <sup>+</sup>	—	
Ni(CN) <sub>5</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	Na <sup>+</sup>	0.25 ± 0.14	
	K <sup>+</sup>	—	
Am(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\epsilon_n$ in NaCl solution for the reactions $An^{3+} + nCO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ ( <i>An</i> = Am, Cm) based on $\epsilon(An^{3+}, Cl^-) = (0.23 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ and $\epsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ .
	Na <sup>+</sup>	-0.23 ± 0.07	
	K <sup>+</sup>	—	
Am(ox) <sub>3</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Estimated in [2005HUM/AND], Section VI.13.2.1 by assuming $\epsilon(Na^+, Am(ox)_3^{3-}) \approx \epsilon(Na^+, Am(CO_3)_3^{3-})$ .
	Na <sup>+</sup>	-0.23 ± 0.10	
	K <sup>+</sup>	—	
Np(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5).
	Na <sup>+</sup>	—	
	K <sup>+</sup>	-0.15 ± 0.07	
NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>	Li <sup>+</sup>	—	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	Na <sup>+</sup>	-0.33 ± 0.17	
	K <sup>+</sup>	—	

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Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$\text{NpO}_2(\text{CO}_3)_2\text{OH}^{3-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.40 \pm 0.19$	Estimated in [2001LEM/FUG] by analogy with $\text{NpO}_2(\text{CO}_3)_3^{4-}$ .
	$\text{K}^+$	—	
$\text{NpO}_2(\text{ox})_2^{3-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.3 \pm 0.2$	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
$\text{NpO}_2\text{edta}^{3-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.20 \pm 0.16$	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
$\text{edta}^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.32 \pm 0.14$	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	$\text{K}^+$	$1.07 \pm 0.19$	
$\text{P}_2\text{O}_7^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.26 \pm 0.05$	Reported by Ciavatta [1988CIA].
	$\text{K}^+$	$-0.15 \pm 0.05$	Reported by Ciavatta [1988CIA].
$\text{Fe}(\text{CN})_6^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	—	
	$\text{K}^+$	$-0.17 \pm 0.03$	
$\text{NpO}_2(\text{CO}_3)_3^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.40 \pm 0.19$	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\text{K}^+$	$-0.62 \pm 0.42$	$\varepsilon(\text{NH}_4^+, \text{NpO}_2(\text{CO}_3)_3^{4-}) = -(0.78 \pm 0.25) \text{ kg}\cdot\text{mol}^{-1}$ is calculated in [2001LEM/FUG] (Section 12.1.2.2.1).
$\text{U}(\text{CO}_3)_4^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.09 \pm 0.10$	These values differ from those estimated in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	—	
$\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.01 \pm 0.11$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	—	

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Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$\text{UO}_2(\text{ox})_3^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.01 \pm 0.11$	Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(\text{Na}^+, \text{UO}_2(\text{ox})_3^{4-}) \approx \varepsilon(\text{Na}^+, \text{UO}_2(\text{CO}_3)_3^{4-})$ .
	$\text{K}^+$	—	
$(\text{UO}_2)_3(\text{OH})_4(\text{SO}_4)_3^{4-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.6 \pm 0.6$	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	$\text{K}^+$	—	
$\text{NpO}_2(\text{CO}_3)_3^{5-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.53 \pm 0.19$	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	$\text{K}^+$	$-0.22 \pm 0.03$	Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from $\Delta\varepsilon$ for the reactions $\text{KNpO}_2\text{CO}_3(\text{s}) + 2\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-} + \text{K}^+$ (in $\text{K}_2\text{CO}_3$ -KCl solution) and $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s}) + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-} + 3\text{K}^+$ (in $\text{K}_2\text{CO}_3$ solution) (based on $\varepsilon(\text{K}^+, \text{CO}_3^{2-}) = (0.02 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ ).
$\text{UO}_2(\text{CO}_3)_3^{5-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.62 \pm 0.15$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	—	
$\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.22 \pm 0.13$	Evaluated in Section XI.1.3.2.1 of [2008RAN/FUG].
	$\text{K}^+$	—	
$\text{Np}(\text{CO}_3)_5^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	—	
	$\text{K}^+$	$-0.73 \pm 0.68$	Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
$(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.46 \pm 0.73$	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\text{K}^+$	—	
$\text{U}(\text{CO}_3)_5^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.30 \pm 0.15$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	$-0.70 \pm 0.31$	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].

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Table B-5: (continued)

$j$	$k$	$\alpha(j,k)$	Comments
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.37 \pm 0.11$	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are based on [1980CIA].
	$\text{K}^+$	—	
$(\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$0.09 \pm 0.71$	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1).
	$\text{K}^+$	—	
$(\text{UO}_2)_5(\text{OH})_8(\text{SO}_4)_4^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$1.10 \pm 0.5$	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	$\text{K}^+$	—	
$\text{Th}(\text{CO}_3)_5^{6-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$-0.30 \pm 0.15$	Estimated in Section XI.1.3.2.1 of [2008RAN/FUG].
	$\text{K}^+$	—	
$(\text{UO}_2)_4(\text{OH})_7(\text{SO}_4)_4^{7-}$	$\text{Li}^+$	—	
	$\text{Na}^+$	$2.80 \pm 0.7$	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	$\text{K}^+$	—	

Table B-6: Ion interaction coefficients,  $\varepsilon_1(j,k)$  and  $\varepsilon_2(j,k)$ , both in  $\text{kg}\cdot\text{mol}^{-1}$ , for cations  $j$  with  $k = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  (first part), and for anions  $j$  with  $k = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  (second part), according to the relationship  $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$  at 298.15 K. The data are taken from Ciavatta [1980CIA], [1988CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level.

$jk \rightarrow$ ↓	$\text{Cl}^-$		$\text{ClO}_4^-$		$\text{NO}_3^-$	
	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$
$\text{NH}_4^+$			$-0.088 \pm 0.002$	$0.095 \pm 0.012$	$-0.075 \pm 0.001$	$0.057 \pm 0.004$
$\text{Tl}^+$			$-0.18 \pm 0.02$	$0.09 \pm 0.02$		
$\text{Ag}^+$					$-0.1432 \pm 0.0002$	$0.0971 \pm 0.0001$
$\text{Pb}^{2+}$					$-0.329 \pm 0.007$	$0.288 \pm 0.018$
$\text{Hg}^{2+}$					$-0.145 \pm 0.001$	$0.194 \pm 0.002$
$\text{Hg}_2^{2+}$					$-0.2300 \pm 0.0004$	$0.194 \pm 0.002$
$jk \rightarrow$ ↓	$\text{Li}^+$		$\text{Na}^+$		$\text{K}^+$	
	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$
$\text{OH}^-$	$-0.039 \pm 0.002$	$0.072 \pm 0.006$				
$\text{NO}_2^-$	$0.02 \pm 0.01$	$0.11 \pm 0.01$				
$\text{NO}_3^-$			$-0.049 \pm 0.001$	$0.044 \pm 0.002$	$-0.131 \pm 0.002$	$0.082 \pm 0.006$
$\text{H}_2\text{PO}_4^-$			$-0.109 \pm 0.001$	$0.095 \pm 0.003$	$-0.1473 \pm 0.0008$	$0.121 \pm 0.004$
$\text{B}(\text{OH})_4^-$			$-0.092 \pm 0.002$	$0.103 \pm 0.005$		
$\text{SO}_3^{2-}$			$-0.125 \pm 0.008$	$0.106 \pm 0.009$		
$\text{SO}_4^{2-}$	$-0.068 \pm 0.003$	$0.093 \pm 0.007$	$-0.184 \pm 0.002$	$0.139 \pm 0.006$		
$\text{S}_2\text{O}_3^{2-}$			$-0.125 \pm 0.008$	$0.106 \pm 0.009$		
$\text{HPO}_4^{2-}$			$-0.19 \pm 0.01$	$0.11 \pm 0.03$	$-0.152 \pm 0.007$	$0.123 \pm 0.016$
$\text{CrO}_4^{2-}$			$-0.090 \pm 0.005$	$0.07 \pm 0.01$	$-0.123 \pm 0.003$	$0.106 \pm 0.007$
$\text{cit}^{3-}$	$-0.55 \pm 0.11^a$	$0.3 \pm 0.2^a$	$-0.15 \pm 0.03^a$	$0.13 \pm 0.03^a$		
$\text{PO}_4^{3-}$			$-0.29 \pm 0.02$	$0.10 \pm 0.01$		

a: See Section VII.3.6 of [2005HUM/AND].

Table B-7: SIT interaction coefficients  $\varepsilon(j,k)$  ( $\text{kg}\cdot\text{mol}^{-1}$ ) for neutral species,  $j$ , with  $k$ , electroneutral combination of ions at 298.15 K.

$j \quad k \rightarrow$ $\downarrow$	$\text{Na}^+ + \text{ClO}_4^-$	$\text{Na}^+ + \text{Cl}^-$	$\text{K}^+ + \text{NO}_3^-$
$\text{H}_2\text{ox}(\text{aq})$	$0.00 \pm 0.01^{\text{b}}$	$0.00 \pm 0.01^{\text{b}}$	$0.00 \pm 0.01^{\text{b}}$
$\text{H}_3\text{cit}(\text{aq})$	$0.00 \pm 0.01^{\text{b}}$	$0.00 \pm 0.01^{\text{b}}$	$0.00 \pm 0.01^{\text{b}}$
$\text{H}_4\text{edta}(\text{aq})$	$-0.29 \pm 0.14$	$-0.29 \pm 0.14$	$-0.29 \pm 0.14$
$\text{SnBr}_2(\text{aq})$	$0.14 \pm 0.07$		
$\text{SnSO}_4(\text{aq})$	$0.19 \pm 0.35$		
$\text{Sn}(\text{NO}_3)_2(\text{aq})$	$0.130 \pm 0.111$		
$\text{Ni}(\text{ox})(\text{aq})$	$-0.07 \pm 0.03$	$-0.07 \pm 0.03$	
$\text{Ni}(\text{Hcit})(\text{aq})$	$-0.07 \pm 0.5$		
$\text{Ni}(\text{SCN})_2(\text{aq})$	$0.38 \pm 0.06^{\text{a}}$		
$\text{Am}(\text{cit})(\text{aq})$		$0.00 \pm 0.05$	
$\text{Np}(\text{edta})(\text{aq})$	$-0.19 \pm 0.19^{\text{e}}$		
$\text{UO}_2\text{ox}(\text{aq})$	$-0.05 \pm 0.06$	$-0.05 \pm 0.06$	
$\text{Uedta}(\text{aq})$	$-0.19 \pm 0.19$		
$\text{Mg}(\text{ox})(\text{aq})$		$0.00 \pm 0.03$	$0.0 \pm 0.1^{\text{c}}$
$\text{Mg}(\text{Hcit})(\text{aq})$	$0.02 \pm 0.05$	$0.02 \pm 0.05$	
$\text{Ca}(\text{ox})(\text{aq})$	$0.0 \pm 0.1^{\text{d}}$	$0.0 \pm 0.1^{\text{c}}$	$0.0 \pm 0.1^{\text{f}}$

(a): See Section V.7.1.3.1 in [2005GAM/BUG].

(b): Basic assumption made in [2005HUM/AND]. See Sections VI.3.5 and VII.3.6 of that review for discussions.

(c): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming  $\alpha(\text{Mg}(\text{ox})(\text{aq}), \text{KNO}_3) \approx \alpha(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(d): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming  $\alpha(\text{Ca}(\text{ox})(\text{aq}), \text{NaClO}_4) \approx \alpha(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(e): Estimated in Section VI.5.1 of [2005HUM/AND] by assuming  $\alpha(\text{Ca}(\text{ox})(\text{aq}), \text{NaCl}) \approx \alpha(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(f): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming  $\alpha(\text{Ca}(\text{ox})(\text{aq}), \text{KNO}_3) \approx \alpha(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(g): Estimated in Section VIII.11.2.2 of [2005HUM/AND] by assuming  $\alpha(\text{Np}(\text{edta})(\text{aq}), \text{NaClO}_4) \approx \alpha(\text{Uedta}(\text{aq}), \text{NaClO}_4)$ .



# Appendix C

## Assigned uncertainties<sup>1</sup>

This appendix describes the origin of the uncertainty estimates that are given in the TDB tables of selected data. The original text in [1992GRE/FUG] has been retained in [1995SIL/BID], [1999RAR/RAN] and [2001LEM/FUG], except for some minor changes. Because of the importance of the uncertainty estimates, the present review offers a more comprehensive description of the procedures used.

### C.1 The general problem

The focus of this section is on the uncertainty estimates of equilibria in solution, where the key problem is analytical, *i.e.*, the determination of the stoichiometric composition and equilibrium constants of complexes that are in rapid equilibrium with one another. We can formulate analyses of the experimental data in the following way: From  $N$  measurements,  $y_i$ , of the variable  $y$  we would like to determine a set of  $n$  equilibrium constants  $k_r$ ,  $r = 1, 2, \dots, n$ , assuming that we know the functional relationship:

$$y = f(k_1, k_2, \dots, k_r, \dots, k_n; a_1, a_2, \dots) \quad (\text{C.1})$$

where  $a_1, a_2, \dots$  are quantities that can be varied but whose values ( $a_{1i}, a_{2i}, \dots$ ) are assumed to be known accurately in each experiment from the data sets ( $y_i, a_{1i}, a_{2i}, \dots$ ),  $i = 1, 2, \dots, N$ . The functional relationship (C.1) is obtained from the chemical model proposed and in general several different models have to be tested before the "best" one is selected. Details of the procedures are given in Rossotti and Rossotti [1961ROS/ROS].

When selecting the functional relationship (C.1) and determining the set of equilibrium constants that best describes the experiments one often uses a least-squares method. Within this method, the "best" description is the one that will minimise the residual sum of squares,  $U$ :

$$U = \sum_i w_i [y_i - f(k_1, \dots, k_n; a_{1i}, a_{2i}, \dots)]^2 \quad (\text{C.2})$$

where  $w_i$  is the weight of each experimental measurement  $y_i$ .

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<sup>1</sup> This appendix essentially contains the text of the TDB-3 Guideline, [1999WAN/OST], earlier versions of which have been printed in all the previous NEA TDB reviews. Because of its importance in the selection of data and to guide the users of the values in Chapters III and IV the text is reproduced here with minor revisions.

The minimum of the function (C.2) is obtained by solving a set of normal equations:

$$\frac{\partial U}{\partial k_r} = 0, r = 1, \dots, n \quad (\text{C.3})$$

A “true” minimum is only obtained if:

- the functional relationship (C.1) is correct, *i.e.*, if the chemical model is correct;
- all errors are random errors in the variable  $y$ , in particular there are no systematic errors;
- the random errors in  $y$  follow a Gaussian (normal) distribution;
- the weight  $w_i(y_i, a_{1i}, a_{2i}, \dots)$  of an experimental determination is an exact measure of its inherent accuracy.

To ascertain that the first condition is fulfilled requires chemical insight, such as information of the coordination geometry, relative affinity between metal ions and various donor atoms, *etc.* It is particularly important to test if the chemical equilibrium constants of complexes that occur in small amounts are chemically reasonable. Too many experimentalists seem to look upon the least-squares refinement of experimental data more as an exercise in applied mathematics than as a chemical venture. One of the tasks in the review of the literature is to check this point. An erroneous chemical model is one of the more serious types of systematic error.

The experimentalist usually selects the variable that he/she finds most appropriate to fulfill the second condition. If the estimated errors in  $a_{1i}, a_{2i} \dots$  are smaller than the error in  $y_i$ , the second condition is reasonably well fulfilled. The choice of the error-carrying variable is a matter of choice based on experience, but one must be aware that it has implications, especially in the estimated uncertainty.

The presence of systematic errors is, potentially, the most important source of uncertainty. There is no possibility to handle systematic errors using statistics; statistical methods may indicate their presence, no more. Systematic errors in the chemical model have been mentioned. In addition there may be systematic errors in the methods used. By comparing experimental data obtained with different experimental methods one can obtain an indication of the presence and magnitude of such errors. The systematic errors of this type are accounted for both in the review of the literature and when taking the average of data obtained with different experimental methods. This type of systematic error does not seem to affect the selected data very much, as judged by the usually very good agreement between the equilibrium data obtained using spectroscopic, potentiometric and solubility methods.



The electrode calibration, especially the conversion between measured pH and  $-\log_{10}[\text{H}^+]$  is an important source of systematic error. The reviewers have when possible corrected this error, as seen in many instances in Appendix A.

The assumption of a normal distribution of the random errors is a choice made in the absence of better alternatives.

Finally, a comment on the weights used in least-squares refinements; this is important because it influences the uncertainty estimate of the equilibrium constants. The weights of individual experimental points can be obtained by repeating the experiment several times and then calculating the average and standard deviation of these data. This procedure is rarely used, instead most experimentalists seem to use unit weight when making a least-squares analysis of their data. However, also in this case there is a weighting of the data by the number of experimental determinations in the parameter range where the different complexes are formed. In order to have comparable uncertainty estimates for the different complexes, one should try to have the same number of experimental data points in the concentration ranges where each of these complexes is predominant; a procedure very rarely used.

As indicated above, the assignment of uncertainties to equilibrium constants is not a straightforward procedure and it is complicated further when there is lack of primary experimental data. The uncertainty estimates given for the individual equilibrium constants reported by the authors and for some cases re-estimated by this review are given in the tables of this and previous reviews. The procedure used to obtain these estimates is given in the original publications and in the Appendix A discussions. However, this uncertainty is still a subjective estimate and to a large extent based on "expert judgment".

## C.2 Uncertainty estimates in the selected thermodynamic data

The uncertainty estimate in the selected thermodynamic data is based on the uncertainty of the individual equilibrium constants or other thermodynamic data, calculated as described in the following sections. A weighted average of the individual  $\log_{10}K$  values is calculated using the estimated uncertainty of the individual experimental values to assign its weight. The uncertainty in this average is then calculated using the formulae given in the following text. This uncertainty depends on the number of experimental data points – for  $N$  data points with the same estimated uncertainty,  $\sigma$ , the uncertainty in the average is  $\sigma/\sqrt{N}$ . The average and the associated uncertainty reported in the tables of selected data are reported with many more digits than justified only in order to allow the users to back-track the calculations. The reported uncertainty is much smaller than the estimated experimental uncertainty and the users of the tables should look at the

discussion of the selected constants in order to get a better estimate of the uncertainty in an experimental determination using a specific method.

One of the objectives of the NEA Thermochemical Database (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, the statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. This appendix outlines the statistical procedures, which were used for fundamentally different problems, and explains the philosophy used in this review when statistics were inapplicable. These rules are followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

### C.3 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points, on which the selected value is based, allows the use of the “root mean square” [1982TAY] deviation of the data points,  $X_i$ , to describe the standard deviation,  $s_X$ , associated with the average,  $\bar{X}$ :

$$s_X = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \bar{X})^2}. \quad (\text{C.4})$$

The standard deviation,  $s_X$ , is thus calculated from the dispersion of the equally weighted data points,  $X_i$ , around the average  $\bar{X}$ , and the probability is 95% that an  $X_i$  is within  $\bar{X} \pm 1.96 s_X$ , see Taylor [1982TAY] (pp. 244-245). The standard deviation,  $s_X$ , is a measure of the precision of the experiment and does not include any systematic errors.

Many authors report standard deviations,  $s_X$ , calculated with Eq. (C.4) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. Therefore, it is thus important not to confuse the standard deviation,  $s_X$ , with the uncertainty,  $\sigma$ . The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors,

$s_j$ , that may be involved. The uncertainty,  $\sigma$ , can be calculated with Eq. (C.5), assuming that the systematic errors are independent.

$$\sigma_X = \sqrt{s_X^2 + \sum_j (s_j^2)} \quad (\text{C.5})$$

The estimation of the systematic errors  $s_j$  (which, of course, have to relate to  $\bar{X}$  and be expressed in the same units) can only be made by a person who is familiar with the experimental method. The uncertainty,  $\sigma$ , has to correspond to the 95% confidence level preferred in this review. It should be noted that for all the corrections and recalculations made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors have to be followed, as outlined in Section C.6.2.

More often, the determination of  $s_X$  is impossible because either only one or two data points are available, or the authors did not report the individual values. The uncertainty  $\sigma$  in the resulting value can still be estimated using Eq. (C.5) assuming that  $s_X^2$  is much smaller than  $\sum_j (s_j^2)$ , which is usually the case anyway.

## C.4 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data,  $X_i$ , are provided with an uncertainty,  $\sigma_i$ , that also includes all systematic errors and represents the 95% confidence level, as described in Section C.3. The weighted mean  $\bar{X}$  and its uncertainty,  $\sigma_{\bar{X}}$ , are then calculated according to Eqs. (C.6) and (C.7).

$$\bar{X} \equiv \frac{\sum_{i=1}^N \left( \frac{X_i}{\sigma_i^2} \right)}{\sum_{i=1}^N \left( \frac{1}{\sigma_i^2} \right)} \quad (\text{C.6})$$

$$\sigma_{\bar{X}} = \sqrt{\frac{1}{\sum_{i=1}^N \left( \frac{1}{\sigma_i^2} \right)}} \quad (\text{C.7})$$

Equations (C.6) and (C.7) may only be used if all the  $X_i$  belong to the same parent distribution. If there are serious discrepancies among the  $X_i$ , one proceeds as described below under Section C.4.1. It can be seen from Eq. (C.7) that  $\sigma_{\bar{X}}$  is directly dependent on the absolute magnitude of the  $\sigma_i$  values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the  $X_i$ , and because the  $\sigma_i$  values already represent the 95% confidence level. The selected uncertainty,  $\sigma_{\bar{X}}$ , will therefore also represent the 95% confidence level.

In cases where all the uncertainties are equal,  $\sigma_i = \sigma$ , Eqs. (C.6) and (C.7) reduce to Eqs. (C.8) and (C.9).

$$\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i \quad (\text{C.8})$$

$$\sigma_{\bar{X}} = \frac{\sigma}{\sqrt{N}} \quad (\text{C.9})$$

### Example C.1:

Five data sources report values for the thermodynamic quantity,  $X$ . The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section C.3.

$i$	$X_i$	$\sigma_i$
1	25.3	0.5
2	26.1	0.4
3	26.0	0.5
4	24.85	0.25
5	25.0	0.6

According to Eqs. (C.6) and (C.7), the following result is obtained:

$$\bar{X} = (25.3 \pm 0.2).$$

The calculated uncertainty,  $\sigma_{\bar{X}} = 0.2$ , appears relatively small, but is statistically correct, as the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.7),  $\sigma_{\bar{X}}$  will always come out smaller than the smallest  $\sigma_i$ . Assuming  $\sigma_4 = 0.10$  instead of 0.25 would yield  $\bar{X} = (25.0 \pm 0.1)$  and  $\sigma_4 = 0.60$  would result in  $\bar{X} = (25.6 \pm 0.2)$ . In fact, the values ( $X_i \pm \sigma_i$ ) in this example are at the limit of consistency, *i.e.*, the range ( $X_4 \pm \sigma_4$ ) does not overlap with the ranges ( $X_2 \pm \sigma_2$ ) and ( $X_3 \pm \sigma_3$ ). There might be a better way to solve this problem. Three possible choices seem more reasonable:

- i. The uncertainties,  $\sigma_i$ , are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the  $\sigma_i$  by 2 would yield  $\bar{X} = (25.3 \pm 0.3)$ .
- ii. If reconsideration of the previous assessments gives no evidence for reassigning the  $X_i$  and  $\sigma_i$  (95% confidence level) values listed above, the statistical conclusion will be that all the  $X_i$  do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for  $i = 1, 4$  and 5 might be considered as belonging to Group A and the values for  $i = 2$  and 3 to Group B. The weighted average of the values in Group A is  $X_A$  ( $i = 1, 4, 5$ ) =  $(24.95 \pm 0.21)$  and of those in Group B,  $X_B$

( $i = 2, 3$ ) =  $(26.06 \pm 0.31)$ , the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under “Discrepancies” (Section C.4.1, Case I).  $X_A$  and  $X_B$  are averaged (straight average, there is no reason for giving  $X_A$  a larger weight than  $X_B$ ), and  $\sigma_{\bar{X}}$  is chosen in such a way that it covers the complete ranges of expectancy of  $X_A$  and  $X_B$ . The selected value is then  $\bar{X} = (25.5 \pm 0.9)$ .

- iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then  $\bar{X} = (25.4 \pm 1.0)$ , which is rounded according to the rules in Section C.6.3 to  $\bar{X} = (25.4 \pm 1.1)$ .

### C.4.1 Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an “outlier”.

**Case I. Two discrepant data:** This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the selected value, because the underlying reason for the discrepancy must be unrecognised systematic errors. There is no point in calculating a weighted average, even if the two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty,  $\sigma_{\bar{X}}$ , assigned to the selected mean,  $\bar{X}$ , has to cover the range of expectation of both source data,  $X_1, X_2$ , as shown in Eq. (C.10),

$$\sigma_{\bar{X}} = |X_i - \bar{X}| + \sigma_{\max} \quad (\text{C.10})$$

where  $i = 1, 2$ , and  $\sigma_{\max}$  is the larger of the two uncertainties  $\sigma_i$ , see Example C.1.ii and Example C.2.

#### Example C.2:

The following credible source data are given:

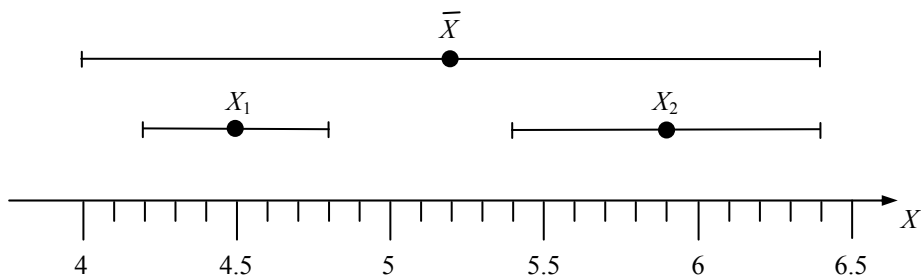
$$X_1 = (4.5 \pm 0.3)$$

$$X_2 = (5.9 \pm 0.5).$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory and there is no justification to discard one of the data. The selected value is then:

$$\bar{X} = (5.2 \pm 1.2).$$

Figure C-1: Illustration for Example C.2.



**Case II. Outliers:** This problem can often be solved by either discarding the outlying data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example C.3 illustrates the procedure.

**Example C.3:**

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

$i$	$X_i$	$\sigma_i$
1	4.45	0.35
2	5.9	0.5
3	5.7	0.4
4	6.0	0.6
5	5.2	0.4

There are two data sets that, statistically, belong to different parent distributions, A and B. According to Eqs. (C.6) and (C.7), the following average values are found for the two groups:  $X_A(i=1) = (4.45 \pm 0.35)$  and  $X_B(i=2, 3, 4, 5) = (5.62 \pm 0.23)$ . The selected value will be the straight average of  $X_A$  and  $X_B$ , analogous to Example C.1:

$$\bar{X} = (5.0 \pm 0.9).$$

## C.5 Several data at different ionic strengths

The extrapolation procedure for aqueous equilibria used in this review is the specific ion interaction model outlined in Appendix B. The objective of this review is to provide selected data sets at standard conditions, *i.e.*, among others, at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the specific ion interaction equations, be extrapolated to  $I = 0$  with a linear regression model, yielding as the intercept the desired equilibrium constant at  $I = 0$ , and as the slope the stoichiometric sum of the ion interaction coefficients,  $\Delta\varepsilon$ . The ion interaction coefficient of the target species can usually be extracted from  $\Delta\varepsilon$  and would be listed in the corresponding table of Appendix B.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to  $I = 0$  should be carried out according to the procedure described in Section C.6.1.

If sufficient data are available at different ionic strengths and in the same inert salt medium, a weighted linear regression will be the appropriate way to obtain both the constant at  $I = 0$ ,  $\bar{X}^\circ$ , and  $\Delta\varepsilon$ . The first step is the conversion of the ionic strength from the frequently used molar ( $\text{mol}\cdot\text{dm}^{-3}$ ,  $M$ ) to the molal ( $\text{mol}\cdot\text{kg}^{-1}$ ,  $m$ ) scale, as described in Section II.2. The second step is the assignment of an uncertainty,  $\sigma_i$ , to each data point  $X_i$  at the molality,  $m_{k,i}$ , according to the rules described in Section C.3. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The subroutine published by Bevington [1969BEV] (pp.104 – 105) has been used for the calculations in the examples of this appendix. Eqs. (C.11) through (C.15) present the equations that are used for the calculation of the intercept  $\bar{X}^\circ$  and the slope  $-\Delta\varepsilon$ :

$$\bar{X}^\circ = \frac{1}{\Delta} \left( \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} \right) \quad (\text{C.11})$$

$$-\Delta\varepsilon = \frac{1}{\Delta} \left( \sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} \right) \quad (\text{C.12})$$

$$\sigma_{\bar{X}^\circ} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2}} \quad (\text{C.13})$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{1}{\sigma_i^2}} \quad (\text{C.14})$$

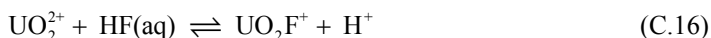
where

$$\Delta = \sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} - \left( \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \right)^2 \quad (\text{C.15})$$

In this way, the uncertainties,  $\sigma_i$ , are not only used for the weighting of the data in Eqs. (C.11) and (C.12), but also for the calculation of the uncertainties,  $\sigma_{\bar{X}^\circ}$  and  $\sigma_{\Delta\varepsilon}$ , in Eqs. (C.13) and (C.14). If the  $\sigma_i$  represents the 95% confidence level,  $\sigma_{\bar{X}^\circ}$  and  $\sigma_{\Delta\varepsilon}$  will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line, but rather directly on their absolute uncertainties,  $\sigma_i$ .

#### Example C.4:

Ten independent determinations of the equilibrium constant,  $\log_{10}^* \beta$ , for the reaction:



are available in  $\text{HClO}_4/\text{NaClO}_4$  media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression,  $(\log_{10}^* \beta + 2D)$  vs.  $m_k$ , according to the formula,  $\log_{10}^* \beta$  (C.16) +  $2D = \log_{10}^* \beta^\circ$  (C.16) -  $\Delta\varepsilon m_k$ , will yield the correct values for the intercept,  $\log_{10}^* \beta^\circ$  (C.16), and the slope,  $\Delta\varepsilon$ . In this case,  $m_k$  corresponds to the molality of  $\text{ClO}_4^-$ .  $D$  is the Debye-Hückel term, *cf.* Appendix B.

$i$	$m_{\text{ClO}_4^-,i}$	$\log_{10}^* \beta + 2D$	$\sigma_i$
1	0.05	1.88	0.10
2	0.25	1.86	0.10
3	0.51	1.73	0.10
4	1.05	1.84	0.10
5	2.21	1.88	0.10
6	0.52	1.89	0.11
7	1.09	1.93	0.11
8	2.32	1.78	0.11
9	2.21	2.03	0.10
10	4.95	2.00	0.32

The results of the linear regression are:

$$\text{intercept} = (1.837 \pm 0.054) = \log_{10}^* \beta^\circ \text{ (C.16)}$$

$$\text{slope} = (0.029 \pm 0.036) = -\Delta\varepsilon.$$

Calculation of the ion interaction coefficient  $\varepsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) = \Delta\varepsilon + \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \varepsilon(\text{H}^+, \text{ClO}_4^-)$ : from  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  (see Appendix B) and the slope of the linear regression,  $\Delta\varepsilon = -(0.03 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ , it follows that  $\varepsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) =$



$(0.29 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ . Note that the uncertainty  $(\pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  is obtained based on the rules of error propagation as described in Section C.6.2:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2} .$$

The resulting selected values are thus:

$$\log_{10} {}^* \beta^\circ (\text{C.16}) = (1.84 \pm 0.05)$$

$$\varepsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) = (0.29 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1} .$$

### C.5.1 Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section C.4. Again, two cases can be defined. Case I: Only two data points are available. Case II: An “outlier” cannot be discarded. If only one data point is available, the procedure for correction to zero ionic strength outlined in Section C.6 should be followed.

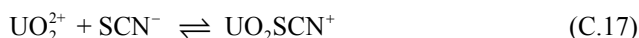
**Case I. Too few molalities:** If only two source data are available, there will be no straightforward way to decide whether or not these two data points belong to the same parent distribution unless either the slope of the straight line is known or the two data refer to the same ionic strength. Drawing a straight line right through the two data points is an inappropriate procedure because all the errors associated with the two source data would accumulate and may lead to highly erroneous values of  $\log_{10} K^\circ$  and  $\Delta\varepsilon$ . In this case, an ion interaction coefficient for the key species in the reaction in question may be selected by analogy (charge is the most important parameter), and a straight line with the slope  $\Delta\varepsilon$  as calculated may then be drawn through each data point. If there is no reason to discard one of the two data points based on the quality of the underlying experiment, the selected value will be the unweighted average of the two standard state data points obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section C.4. It should be mentioned that the ranges of expectancy of the corrected values at  $I = 0$  are given by their uncertainties, which are based on the uncertainties of the source data at  $I \neq 0$  and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate, but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section C.6.2. The ion interaction coefficients estimated by analogy are listed in the table of selected ion interaction coefficients (Appendix B), but they are flagged as estimates.

**Case II. Outliers and inconsistent data sets:** This case includes situations where it is difficult to decide whether or not a large number of points belong to the same parent distribution. There is no general rule on how to solve this problem, and decisions are left to the judgment of the reviewer. For example, if eight data points follow a straight line reasonably well and two lie way out, it may be justified to discard the “outliers”. If, however, the eight points are scattered considerably and two points are just a

bit further out, one can probably not consider them as “outliers”. It depends on the particular case and on the judgment of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope,  $\Delta\varepsilon$ , of the straight line should be estimated by analogy.

### Example C.5:

Six reliable determinations of the equilibrium constant,  $\log_{10} \beta$ , of the reaction:



are available in different electrolyte media:

$$I_c = 0.1 \text{ M (KNO}_3) \quad \log_{10} \beta (\text{C.17}) = (1.19 \pm 0.03)$$

$$I_c = 0.33 \text{ M (KNO}_3) \quad \log_{10} \beta (\text{C.17}) = (0.90 \pm 0.10)$$

$$I_c = 1.0 \text{ M (NaClO}_4) \quad \log_{10} \beta (\text{C.17}) = (0.75 \pm 0.03)$$

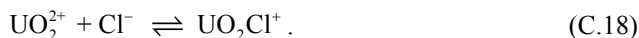
$$I_c = 1.0 \text{ M (NaClO}_4) \quad \log_{10} \beta (\text{C.17}) = (0.76 \pm 0.03)$$

$$I_c = 1.0 \text{ M (NaClO}_4) \quad \log_{10} \beta (\text{C.17}) = (0.93 \pm 0.03)$$

$$I_c = 2.5 \text{ M (NaNO}_3) \quad \log_{10} \beta (\text{C.17}) = (0.72 \pm 0.03)$$

The uncertainties are assumed to represent the 95% confidence level. From the values at  $I_c = 1 \text{ M}$ , it can be seen that there is a lack of consistency in the data, and that a linear regression similar to that shown in Example C.4 would be inappropriate. Instead, the use of  $\Delta\varepsilon$  values from reactions of the same charge type is encouraged. Analogies with  $\Delta\varepsilon$  are more reliable than analogies with single  $\varepsilon$  values due to canceling effects. For the same reason, the dependency of  $\Delta\varepsilon$  on the type of electrolyte is often smaller than for single  $\varepsilon$  values.

A reaction of the same charge type as Reaction (C.17), and for which  $\Delta\varepsilon$  is well known, is:



The value of  $\Delta\varepsilon (\text{C.18}) = -(0.25 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  was obtained from a linear regression using 16 experimental values between  $I_c = 0.1 \text{ M}$  and  $I_c = 3 \text{ M Na(Cl,ClO}_4)$  [1992GRE/FUG]. It is thus assumed that:

$$\Delta\varepsilon (\text{C.17}) = \Delta\varepsilon (\text{C.18}) = -(0.25 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}.$$

The correction of  $\log_{10} \beta (\text{C.17})$  to  $I = 0$  is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10} \beta + 4D = \log_{10} \beta^\circ - \Delta\varepsilon I_m \quad (\text{C.19})$$

$D$  is the Debye-Hückel term and  $I_m$  the ionic strength converted to molal units by using the conversion factors listed in Table II-5. The following list gives the details

of this calculation. The resulting uncertainties in  $\log_{10} \beta$  are obtained based on the rules of error propagation as described in Section C.6.2.

Table C-1: Details of the calculation of the equilibrium constant for Reaction (C.17) corrected to  $I = 0$ , using (C.19).

$I_m$	electrolyte	$\log_{10} \beta$	$4D$	$\Delta\varepsilon I_m$	$\log_{10} \beta^\circ$
0.101	KNO <sub>3</sub>	(1.19 ± 0.03)	0.438	-0.025	(1.68 ± 0.03) <sup>a</sup>
0.335	KNO <sub>3</sub>	(0.90 ± 0.10)	0.617	-0.084	(1.65 ± 0.10) <sup>a</sup>
1.050	NaClO <sub>4</sub>	(0.75 ± 0.03)	0.822	-0.263	(1.31 ± 0.04)
1.050	NaClO <sub>4</sub>	(0.76 ± 0.03)	0.822	-0.263	(1.32 ± 0.04)
1.050	NaClO <sub>4</sub>	(0.93 ± 0.03)	0.822	-0.263	(1.49 ± 0.04)
2.714	NaNO <sub>3</sub>	(0.72 ± 0.03)	0.968	-0.679	(1.82 ± 0.13) <sup>a</sup>

- a: These values were corrected for the formation of the nitrate complex,  $\text{UO}_2\text{NO}_3^+$ , by using  $\log_{10} \beta^\circ(\text{UO}_2\text{NO}_3^+) = (0.30 \pm 0.15)$  [1992GRE/FUG].

As was expected, the resulting values,  $\log_{10} \beta^\circ$ , are inconsistent and have therefore to be treated as described in Case I of Section C.4. That is, the selected value will be the unweighted average of  $\log_{10} \beta^\circ$ , and its uncertainty will cover the entire range of expectancy of the six values. A weighted average would only be justified if the six values of  $\log_{10} \beta^\circ$  were consistent. The result is:

$$\log_{10} \beta^\circ = (1.56 \pm 0.39).$$

## C.6 Procedures for data handling

### C.6.1 Correction to zero ionic strength

The correction of experimental data to zero ionic strength is necessary in all cases where a linear regression is impossible or appears inappropriate. The method used throughout the review involves application of the specific ion interaction equations described in detail in Appendix B. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95% confidence level: the experimental source value,  $\log_{10} K$  or  $\log_{10} \beta$ , and the stoichiometric sum of the ion interaction coefficients,  $\Delta\varepsilon$ . The ion interaction coefficients (see Tables B-4, B-5, B-6 and B-7 of Appendix B) required to calculate  $\Delta\varepsilon$  may not all be known. Missing values therefore need to be estimated. It is recalled that the electric charge has the most significant influence on the magnitude of the ion interaction coefficients, and that it is in general more reliable to estimate  $\Delta\varepsilon$  from known reactions of the same charge type, rather than to estimate single  $\varepsilon$  values. The uncertainty of the corrected value at  $I = 0$  is calculated by taking into account the propagation of errors, as described below. It should be noted

that the ionic strength is frequently given in moles per dm<sup>3</sup> of solution (molar, M) and has to be converted to moles per kg H<sub>2</sub>O (molal, *m*), as the model requires. Conversion factors for the most common inert salts are given in Table II.5.

### Example C.6:

For the equilibrium constant of the reaction:



only one credible determination in 3 M NaClO<sub>4</sub> solution is known to be,  $\log_{10} {}^* \beta (C.20) = -6.31$ , to which an uncertainty of  $\pm 0.12$  has been assigned. The ion interaction coefficients are as follows:

$$\varepsilon(M^{3+}, ClO_4^-) = (0.56 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1},$$

$$\varepsilon(M(OH)_2^+, ClO_4^-) = (0.26 \pm 0.11) \text{ kg}\cdot\text{mol}^{-1},$$

$$\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}.$$

The values of  $\Delta\varepsilon$  and  $\sigma_{\Delta\varepsilon}$  can be obtained readily (*cf.* Eq. (C.22)):

$$\Delta\varepsilon = \varepsilon(M(OH)_2^+, ClO_4^-) + 2\varepsilon(H^+, ClO_4^-) - \varepsilon(M^{3+}, ClO_4^-) = -0.22 \text{ kg}\cdot\text{mol}^{-1},$$

$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2 \times 0.02)^2 + (0.03)^2} = 0.12 \text{ kg}\cdot\text{mol}^{-1}.$$

The two variables are thus:

$$\log_{10} {}^* \beta (C.20) = -(6.31 \pm 0.12),$$

$$\Delta\varepsilon = -(0.02 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}.$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10} {}^* \beta (C.20) + 6D = \log_{10} {}^\circ \beta (C.20) - \Delta\varepsilon m_{ClO_4^-}$$

*D* is the Debye-Hückel term:

$$D = \frac{0.509\sqrt{I_m}}{(1 + 1.5\sqrt{I_m})}.$$

The ionic strength, *I<sub>m</sub>*, and the molality, *m<sub>ClO<sub>4</sub><sup>-</sup></sub>* (*I<sub>m</sub>*  $\approx$  *m<sub>ClO<sub>4</sub><sup>-</sup></sub>*), have to be expressed in molal units, 3 M NaClO<sub>4</sub> corresponding to 3.5 m NaClO<sub>4</sub> (see Section II.2), giving *D* = 0.25. This results in:

$$\log_{10} {}^\circ \beta (C.20) = -4.88.$$

The uncertainty in  $\log_{10} {}^\circ \beta$  is calculated from the uncertainties in  $\log_{10} {}^* \beta$  and  $\Delta\varepsilon$  (*cf.* Eq. (C.22)):

$$\sigma_{\log_{10} {}^\circ \beta} = \sqrt{\sigma_{\log_{10} {}^* \beta}^2 + (m_{ClO_4^-} \sigma_{\Delta\varepsilon})^2} = \sqrt{(0.12)^2 + (3.5 \times 0.12)^2} = 0.44$$

The selected, rounded value is:

$$\log_{10} {}^* \beta^\circ (\text{C.20}) = -(4.9 \pm 0.4).$$

## C.6.2 Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A clear outline of the propagation of errors is given by Bevington [1969BEV]. A simplified form of the general formula for error propagation is given by Eq. (C.21), supposing that  $X$  is a function of  $Y_1, Y_2, \dots, Y_N$ .

$$\sigma_X^2 = \sum_{i=1}^N \left( \frac{\partial X}{\partial Y_i} \sigma_{Y_i} \right)^2 \quad (\text{C.21})$$

Equation (C.21) can be used only if the variables,  $Y_1, Y_2, \dots, Y_N$ , are independent or if their uncertainties are small, *i.e.*, the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (C.21) can thus almost universally be used in this review. Eqs. (C.22) through (C.26) present explicit formulae for a number of frequently encountered algebraic expressions, where  $c, c_1, c_2$  are constants.

$$X = c_1 Y_1 \pm c_2 Y_2 : \quad \sigma_X^2 = (c_1 \sigma_{Y_1})^2 + (c_2 \sigma_{Y_2})^2 \quad (\text{C.22})$$

$$X = \pm c Y_1 Y_2 \text{ and } X = \pm \frac{c Y_1}{Y_2} : \quad \left( \frac{\sigma_X}{X} \right)^2 = \left( \frac{\sigma_{Y_1}}{Y_1} \right)^2 + \left( \frac{\sigma_{Y_2}}{Y_2} \right)^2 \quad (\text{C.23})$$

$$X = c_1 Y^{\pm c_2} : \quad \frac{\sigma_X}{X} = c_2 \frac{\sigma_Y}{Y} \quad (\text{C.24})$$

$$X = c_1 e^{\pm c_2 Y} : \quad \frac{\sigma_X}{X} = c_2 \sigma_Y \quad (\text{C.25})$$

$$X = c_1 \ln(|c_2 Y|) : \quad \sigma_X = c_1 \frac{\sigma_Y}{Y} \quad (\text{C.26})$$

### Example C.7:

A few simple calculations illustrate how these formulae are used. The values have not been rounded.

$$\begin{aligned} \text{Eq. (C.22)} : \quad \Delta_r G_m &= 2[-(277.4 \pm 4.9)] \text{ kJ}\cdot\text{mol}^{-1} - [-(467.3 \pm 6.2)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -(87.5 \pm 11.6) \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

$$\text{Eq. (C.23)} : \quad K = \frac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.96)$$

$$\text{Eq. (C.24)} : K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$$

$$\text{Eq. (C.25)} : K^\circ = e^{\frac{-\Delta_r G_m^\circ}{RT}} ; \quad \Delta_r G_m^\circ = -(2.7 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T = 298.15 \text{ K}$$

$$K^\circ = (2.97 \pm 0.36).$$

Note that powers of 10 have to be reduced to powers of  $e$ , *i.e.*, the variable has to be multiplied by  $\ln(10)$ , *e.g.*,

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10) \cdot \log_{10} K)} = (282 \pm 65).$$

$$\text{Eq. (C.26)} : \quad \Delta_r G_m^\circ = -RT \ln K^\circ; \quad K^\circ = (8.2 \pm 1.2) \times 10^6$$

$$R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T = 298.15 \text{ K}$$

$$\Delta_r G_m^\circ = -(39.46 \pm 0.36) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\ln K^\circ = (15.92 \pm 0.15)$$

$$\log_{10} K^\circ = \ln K^\circ / \ln(10) = (6.91 \pm 0.06).$$

Again, it can be seen that the uncertainty in  $\log_{10} K^\circ$  cannot be the same as in  $\ln K^\circ$ . The constant conversion factor of  $\ln(10) = 2.303$  is also to be applied to the uncertainty.

### C.6.3 Rounding

The standard rules to be used for rounding are:

1. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.
2. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.
3. When the digit following the last digit to be retained is 5 and
  - a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged;
  - b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations are carried out in full, and only the final results are rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected data set is developed, and only then are data rounded.

#### C.6.4 Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

Example:  $(3.478 \pm 0.008)$

$(3.48 \pm 0.01)$

$(2.8 \pm 0.4)$

$(10 \pm 1)$

$(105 \pm 20)$ .

In the case of auxiliary data or values that are used for later calculations, it is often inconvenient to round to the last significant digit. In the value  $(4.85 \pm 0.26)$ , for example, the “5” is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.





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This chapter contains an alphabetical list of the authors of the references cited in this book. The reference codes given with each name correspond to the publications of which the person is the author or a co-author. Note that inconsistencies may occur due to a variation in spelling between different publications. No attempt was made to correct for such inconsistencies in this volume.

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Hager, D.	[2000LOT/OCH]
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Holmström, B.	[2007COH/CVI]

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Lorimer, J. W.	[2003LOR], [2008GAM/LOR]
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Lusardi, W.	[2004DUN/CRA]
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Marquardt, R.	[2007COH/CVI]
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Takami, M.	[2007COH/CVI]
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Takeshita, M.	[1984ICH/TAK]
Tanaka, I.	[2008SEK/TOG], [2010TAN/SEK]
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This volume is the 12<sup>th</sup> in the OECD Nuclear Energy Agency (NEA) “Chemical Thermodynamics” series. It is based on a critical review of the thermodynamic properties of tin, its solid compounds and aqueous complexes, carried out as part of the NEA Thermochemical Database Project Phase III (TDB III). The database system developed at the OECD/NEA Data Bank ensures consistency not only within the recommended data sets of tin, but also among all the data sets published in the series. This volume will be of particular interest to scientists carrying out performance assessments of deep geological disposal sites for radioactive waste.

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**ISBN 978-92-64-99206-1**

